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Introduction to neutron reflection

Adrian Rennie

Outline

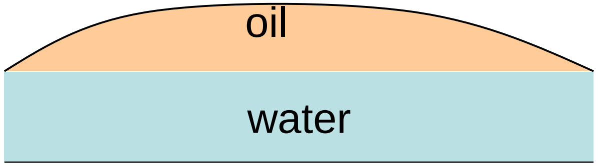
Inteference of waves

Refractive index

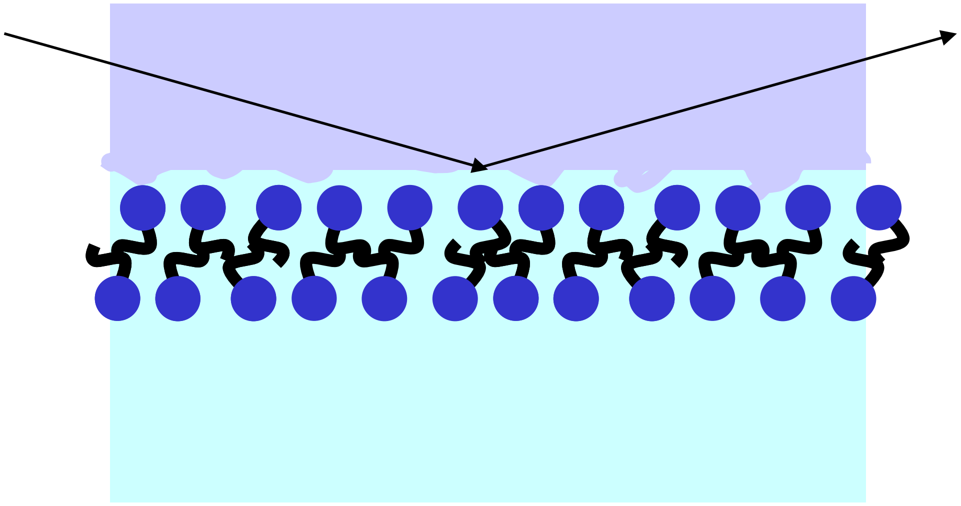
Critical angle, total reflection

Reflection

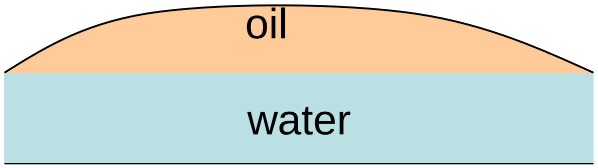
Light



Reflection



Light

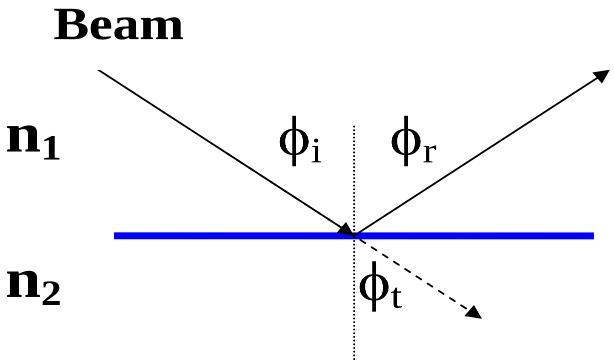


Why neutrons?

Contrast: light elements, isotopes
Penetrate
Magnetism

Reflection and Refraction: Snell's Law

Optical Notation



For specular reflection:

$$\phi_i = \phi_r$$

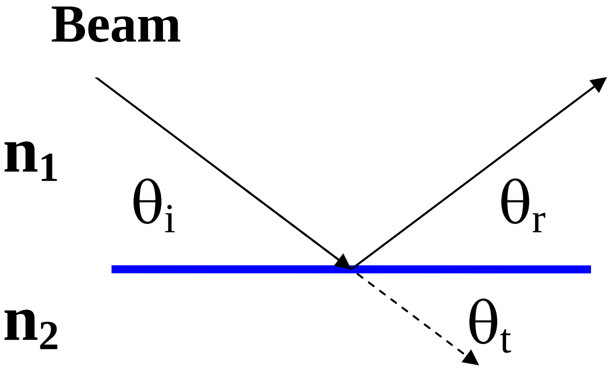
Transmitted beam is refracted:

$$n_2 \sin \phi_t = n_1 \sin \phi_i$$

n is refractive index

Reflection and Refraction: Snell’s Law

Neutron Reflection Notation



$\theta = 90° - \varphi$

For specular reflection:

$\theta_i = \theta_r$

Transmitted beam is refracted:

$n_2 \cos \theta_t = n_1 \cos \theta_i$

n is refractive index

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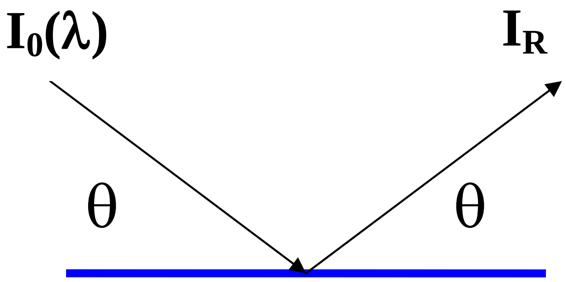
Reflection – measured quantities

Reflection



Reflected beam deflected: $2\,\theta$

Reflectivity

$R(Q) = I_R/I_0(\lambda)$

Momentum transfer

$Q = (4\pi/\lambda) \sin\theta$

Demonstration Calculations

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www.ncnr.nist.gov/instruments/magik/calculators/reflectivity-calculator.html

www.ncnr.nist.gov/instruments/magik/calculators/magnetic-reflectivity-calculator.html

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Critical Angle and Below (critical wavelength and above)

Density difference between two bulk phases determines the critical momentum transfer/angle, Q_c or θ_c

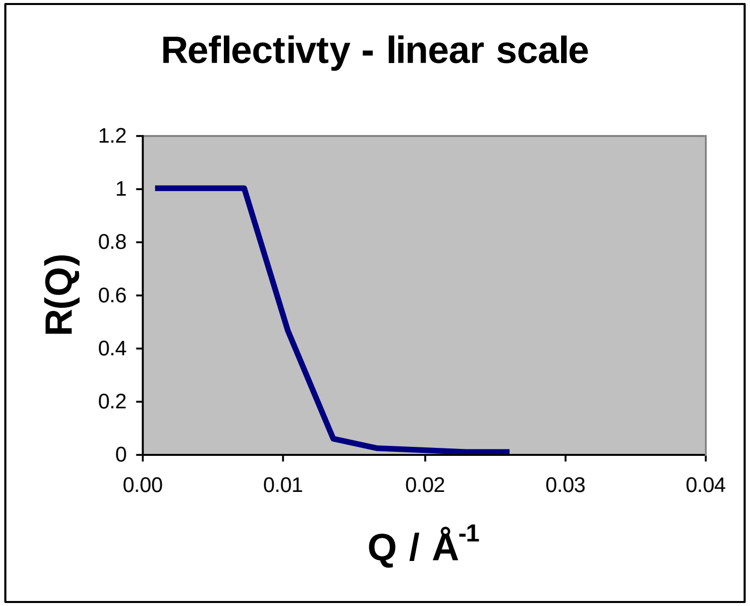
Any variation in intensity below critical angle is probably telling you about the experiment rather than the interface

R (Q) = 1 for $\theta < \theta_c$ is often used as a calibrant

$R(Q) \sim 1/Q^4$ for sharp interface

Total reflection below critical angle θ

$\cos \theta = n_2/n_1$



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Calculating Refractive Index

Neutrons

$$n = 1 - (\lambda^2 \Sigma_i b_i/V / 2\pi)$$

λ is the wavelength

$\Sigma_i b_i$ is the sum of scattering lengths in volume V

b is known for most stable nuclei

$\rho = \Sigma_i b_i/V$

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Scattering Lengths of Nuclei

Nucleus	Scattering Length / fm
^{1}H	-3.741
^{2}H (or D)	6.675
C	6.648
O	5.805
Si	4.151
Cl	9.579

Source: H. Rauch & W. Waschkowski

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Properties of Common Materials

Material	Scatt. Length Density / 10^{-6} Å^{-2}	Refractive index at 10 Å
H_2O	-0.56	1.000009
D_2O	6.35	0.999899
Si	2.07	0.999967
Air	0	1.000000
Polystyrene	1.4	0.999971

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Contrast in a Thin Film

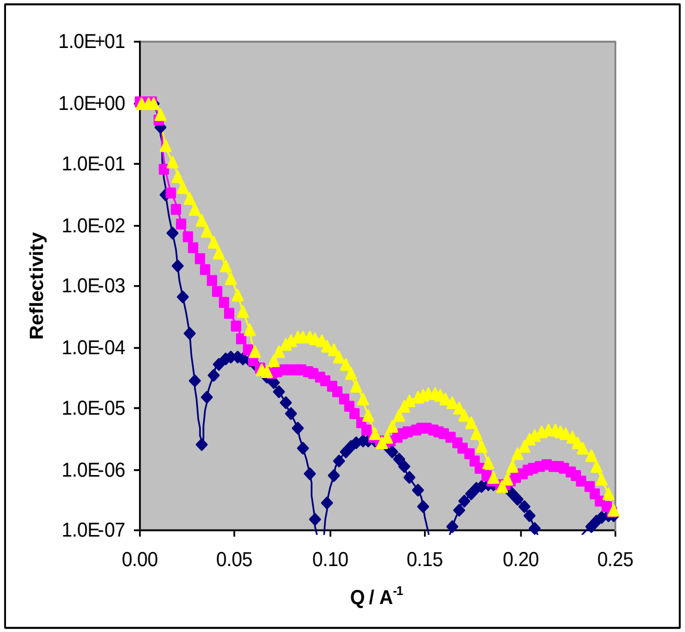
Calculation for Neutrons

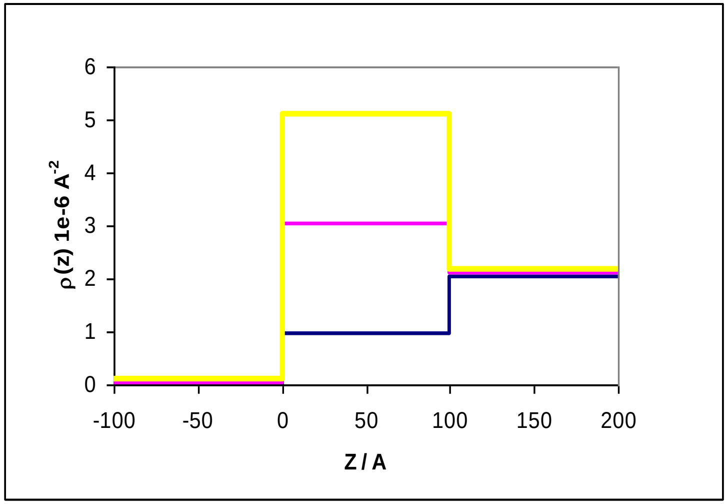
100 Å layer with ρ=1, 3 & 5 x 10^{-6} Å^{-2}
on Si (ρ=2.07 x 10^{-6} Å^{-2})

Increasing contrast changes visibility of fringes

Phase change makes large difference

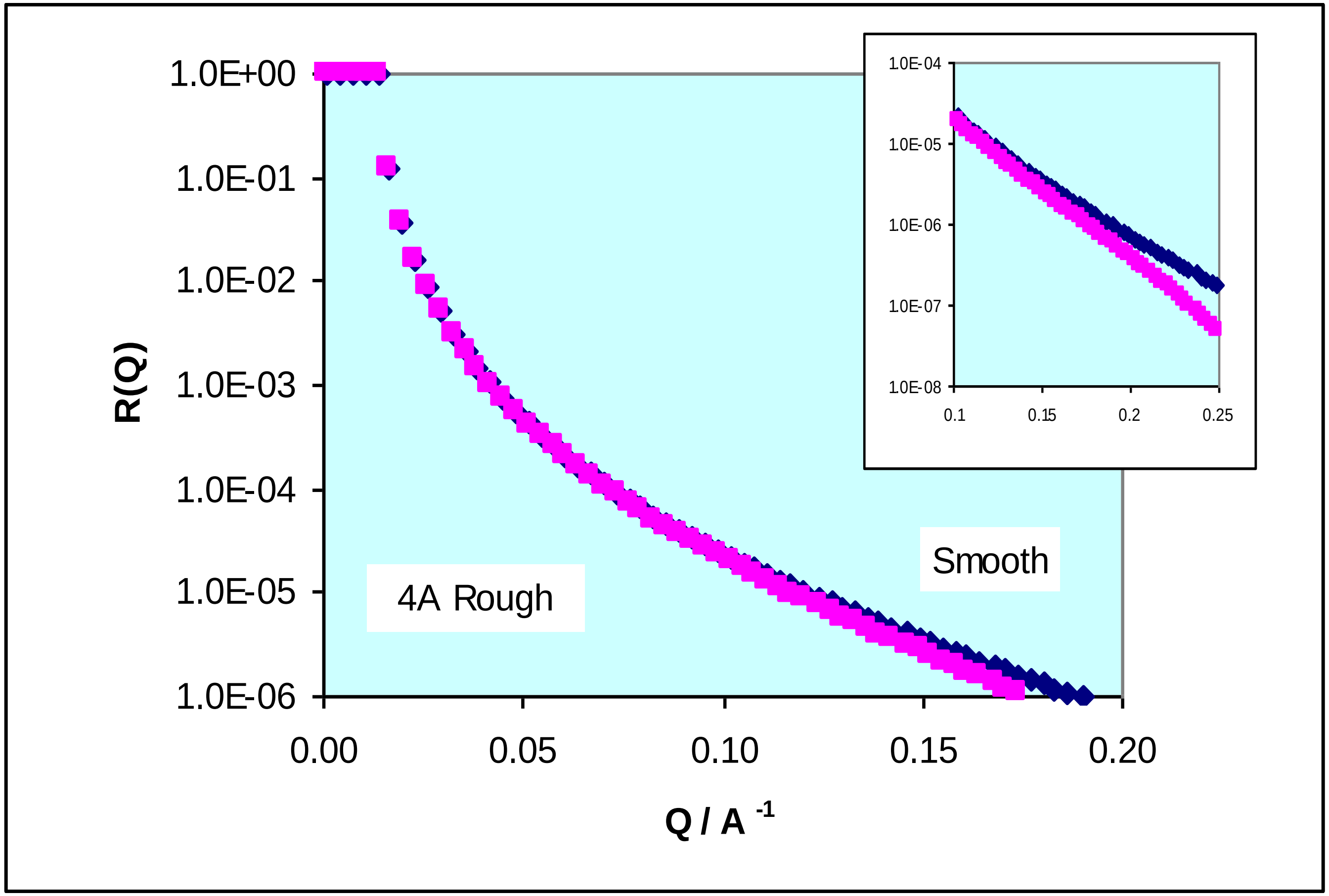
Fringes (Kiessig fringes) – spacing indicates film thickness for a single layer.





Roughness

Reflectivity from rough surfaces is decreased.



L. Nevot, P. Crocé *J. Phys. Appl.* **15**, T61 (1980)

Intensity of Reflected Signal

Waves interfere constructively for

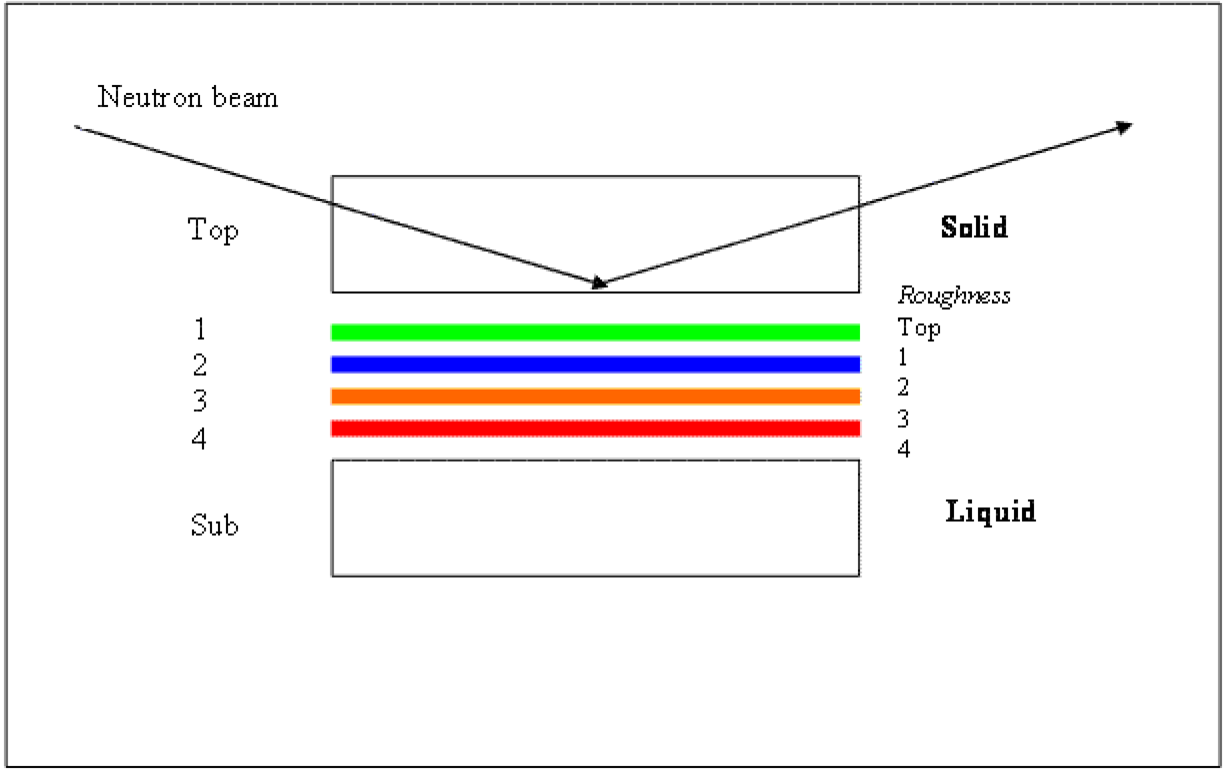
$2\ d \sin \theta = \lambda, 2\lambda, 3\lambda\ \ldots$ (Bragg's law)

Measured reflectivity will depend on angle and wavelength.

Total reflection for angles less than critical angle, $\theta_c = \arccos(n_1/n_2)$

Useful Physical Ideas

Models for complex interfaces can be constructed from multiple thin layers of different refractive index, n or scattering length density, ρ.



Useful Physical Ideas

Isotopes (e.g. D/H substitution) can be used to label particular species or alter contrast

Neutrons have spin – effectively a field dependent contribution to scattering length

Abeles Optical Matrix Method

$$r_j = \begin{bmatrix} e^{i\beta_{j-1}} & r_{j-1}e^{i\beta_{j-1}} \\ r_{j-1}e^{-i\beta_{j-1}} & e^{-i\beta_{j-1}} \end{bmatrix}$$

$$\beta_j = (2\pi/\lambda)n_j d_j \sin\theta_j \qquad p_j = n_j \sin\theta_j$$

$$r_j = (p_{j-1} - p_j)/(p_{j-1} + p_j) \qquad M_R = [M_1][M_2]...[M_{n-1}]$$

$$R(Q) = M_{21}M_{21}{}^{*}/M_{11}M_{11}{}^{*}$$

Magnetic Contrast

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$b_m = \mu_0 \, e^2 \, S \, \gamma \, / \, 4\pi \, m_e$

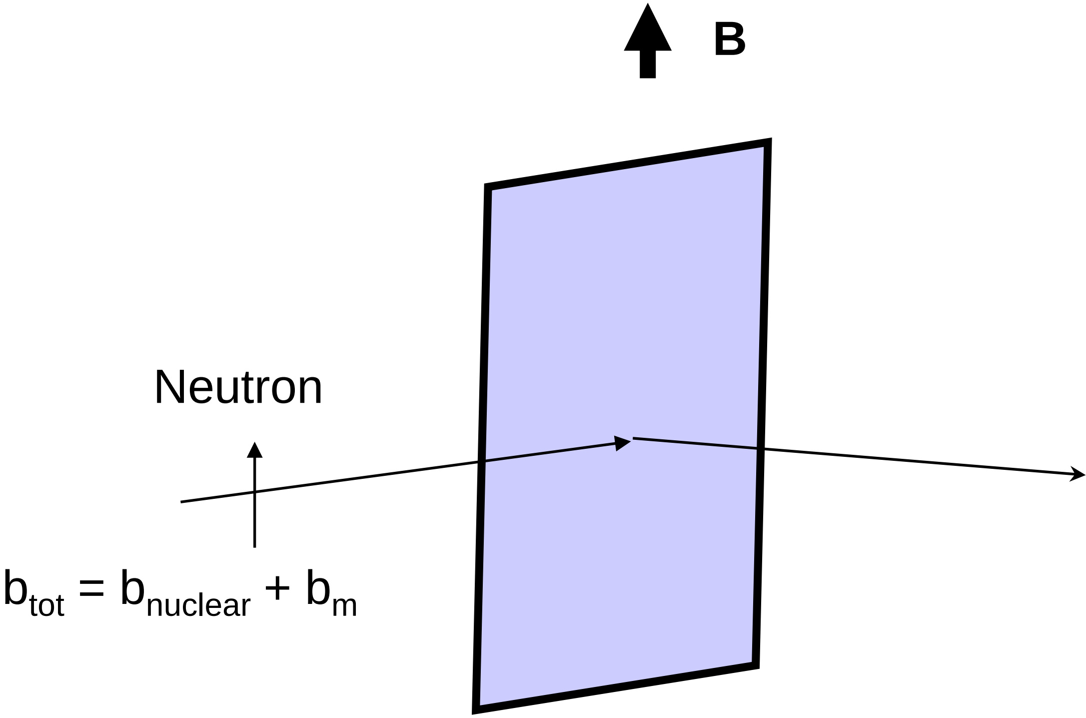
e, electronic charge

m_e, electron mass

S, spin

$\mu_{0,}$ Permeability of free space

γ, gyromagnetic ratio, 1.913



$b_{tot} = b_{nuclear} \pm b_m$

Magnetic Contrast

$b_m = \mu_0 \, e^2 \, S \, \gamma \, / \, 4\pi \, m_e$

e, electronic charge

m_e, electron mass

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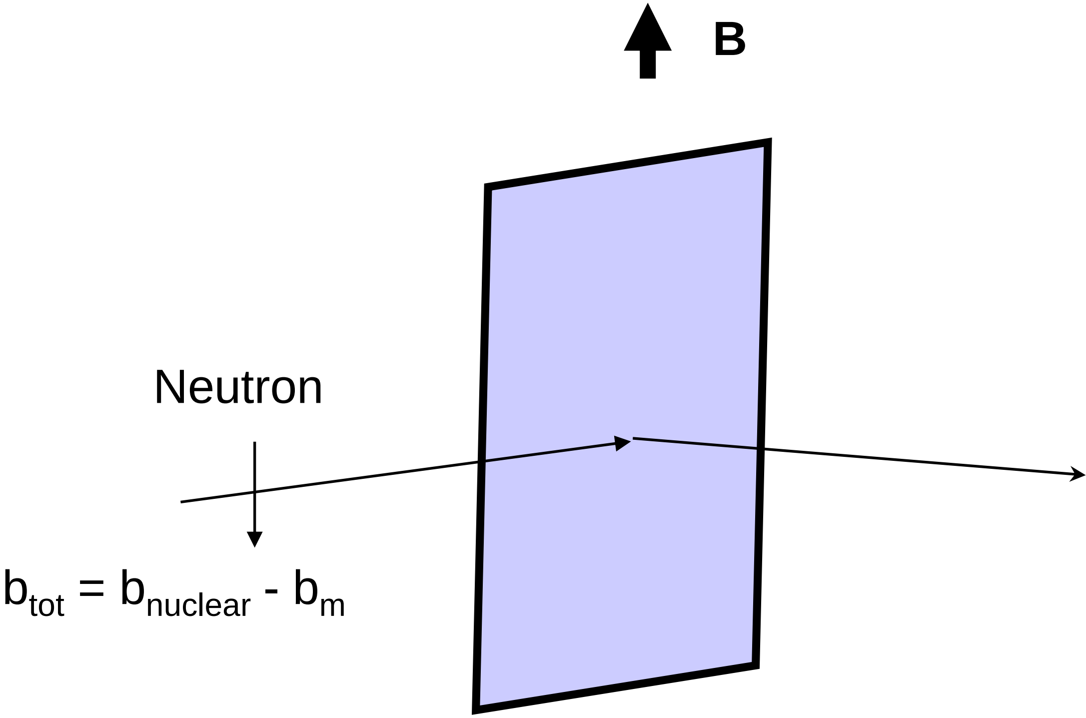
$b_{tot} = b_{nuclear} \pm b_m$



Scattering and Reflection

ρ(Q) is Fourier transform of the scattering length density distribution normal to the interface, ρ(z)

$$R(Q) = \frac{16\pi^2}{Q^2}\left|\rho(Q)\right|^2$$

$$\rho(\mathrm{Q}) = \int_{-\infty}^{\infty} \rho(\mathrm{z})\mathrm{e}^{-\mathrm{iQz}}\mathrm{dz}$$

For sharp interface:

$R(Q) \sim 1/Q^4$

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Partial Structure Factors

Interface consists of distinct components: *1, 2, 3*

$$R(Q)=\frac{16\pi^2}{Q^2}\,|\int \rho(z)e^{iQz}dz\,|^2$$

$$\rho(z)=b_1n_1(z)+b_2n_2(z)+b_3n_3(z)$$

$$R(Q)=\frac{16\pi^2}{Q^2}(b_1^2h_{11}+2b_1b_2h_{12}+b_2^2h_{22}+2b_2b_3h_{23}+b_3^2h_{33}+2b_3b_1h_{31})$$

h_{ij} are transforms of n_in_j – pair correlation functions

Lu, J. R.; Thomas, R. K.; Penfold, J. *Adv. Coll. Inter. Sci.* **2000**, 84, 143-304.

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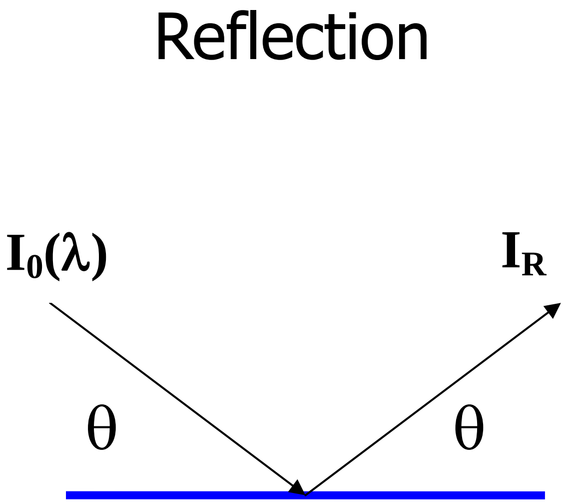
Practical Aspects of Neutron Reflection

How to Collect Data

Adrian R. Rennie

Reflection – measured quantities



Reflected beam deflected:

$2\,\theta$

Reflectivity

$R(\theta, \lambda) = I_R/I_0(\lambda)$

Momentum transfer

$Q = (4\pi/\lambda) \sin\theta$

Best Sources of Neutrons

ILL reactor continuous

Thermal Flux 1.5 x 10^{15} n cm^{-2} s^{-1}

SNS, ORNL

60 Hz, 300 μs

5 x 10^{17} n cm^{-2} s^{-1} (Peak)

Neutrons: Speed & Wavelength

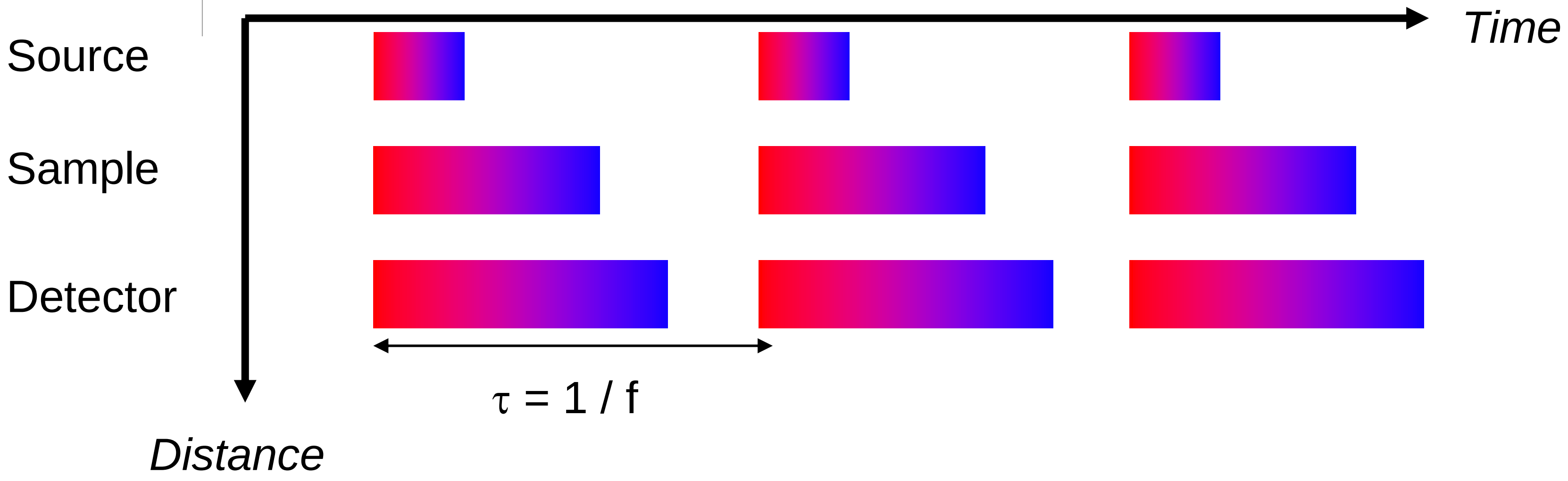
Velocity, v, from de Broglie relation

$$v \lambda = 3956 \text{ m s}^{-1} \text{ Å}$$

i.e. 10 Å has 400 m s^{-1}

Gravity is significant, separate wavelengths mechanically

Using a Pulsed Source



Time

Source

Sample

Detector

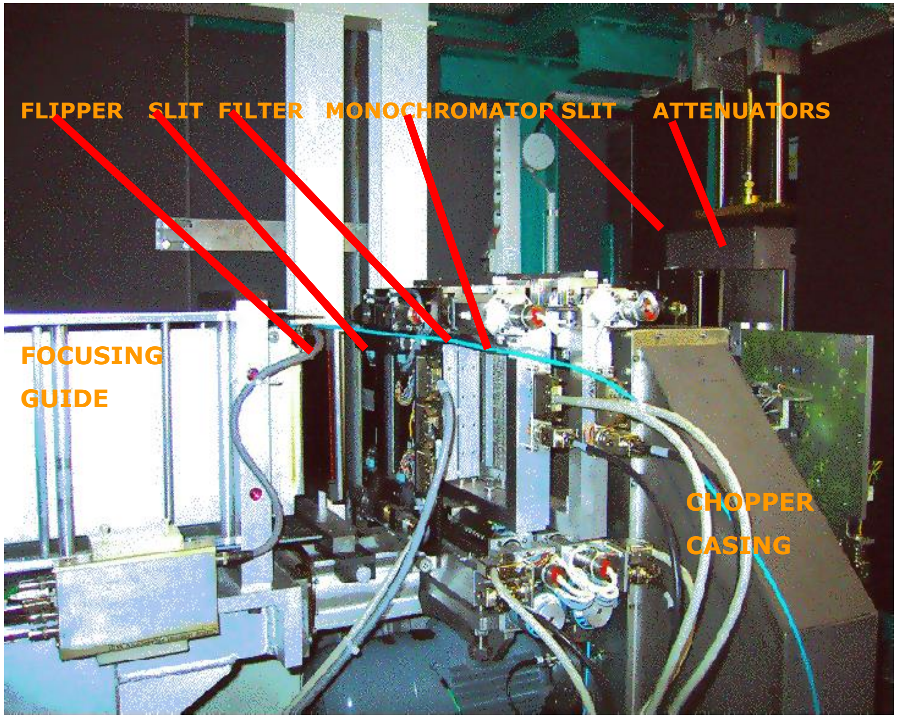
$\tau = 1 / f$

Distance

Detection time (after source pulse) gives wavelength

Choppers can select a wavelength

D17 Reflectometer



Practical Issues

Reflectivity drops quickly with increasing Q (or angle). Signal is easily ‘lost’ in background.

To observe fringes it will be necessary to measure over an appropriate range of Q and to have sufficient resolution (ΔQ small enough).

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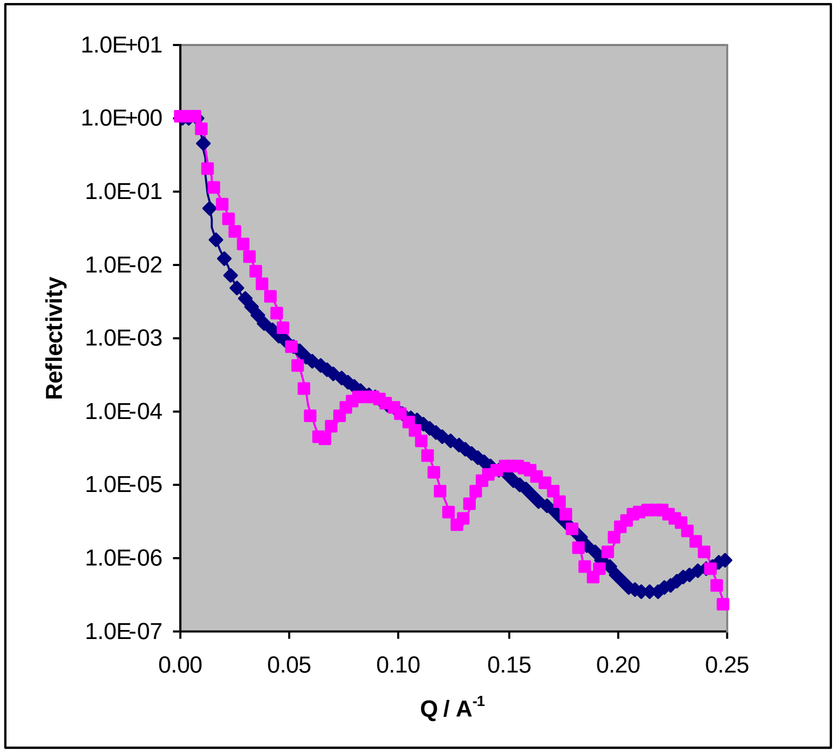
Reflection from a Thin Film

Model calculation on smooth surface.

Fringe spacing depends on thickness

Fringe spacing ~ $2\pi/d$



Model layer with ρ = 5 x 10^{-6} Å^2 on Si (2.07 x 10^{-6} Å $^{-2}$) Blue 30 Å, Pink 100 Å. No roughness.

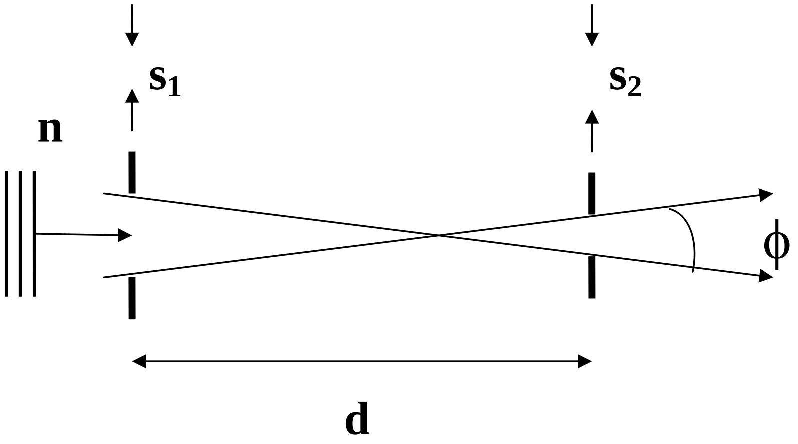
Resolution in Q

$Q = (4\pi/\lambda) \sin \theta$

Depends on $\Delta\lambda$ and $\Delta\theta$

Angle resolution, $\Delta\theta$, depends on collimation (slits)

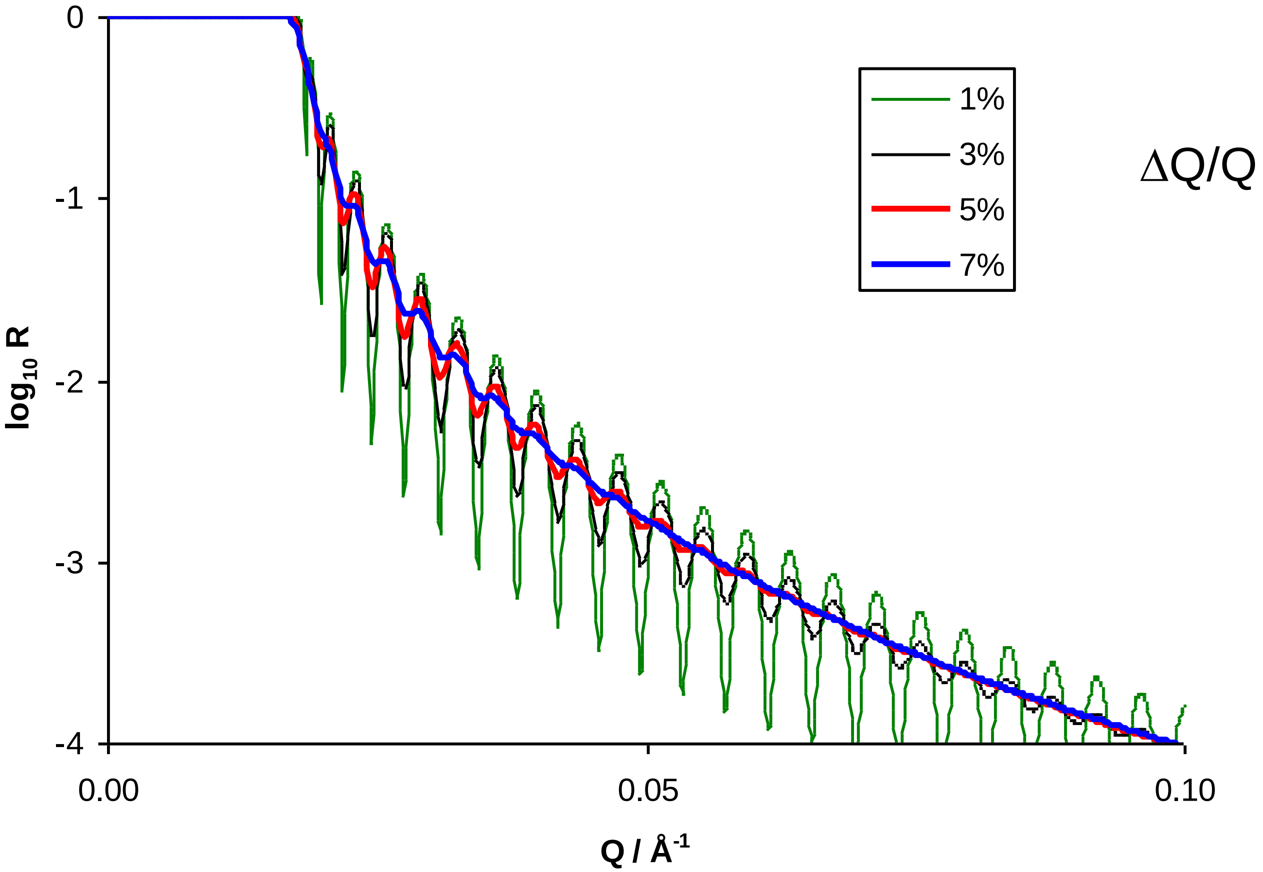
Wavelength resolution depends on monochromator or time resolution in measuring neutron pulse



Higher Resolution = Lower Flux

$$(\Delta Q/Q)^2 = (\Delta\lambda/\lambda)^2 + (\Delta\theta/\theta)^2$$

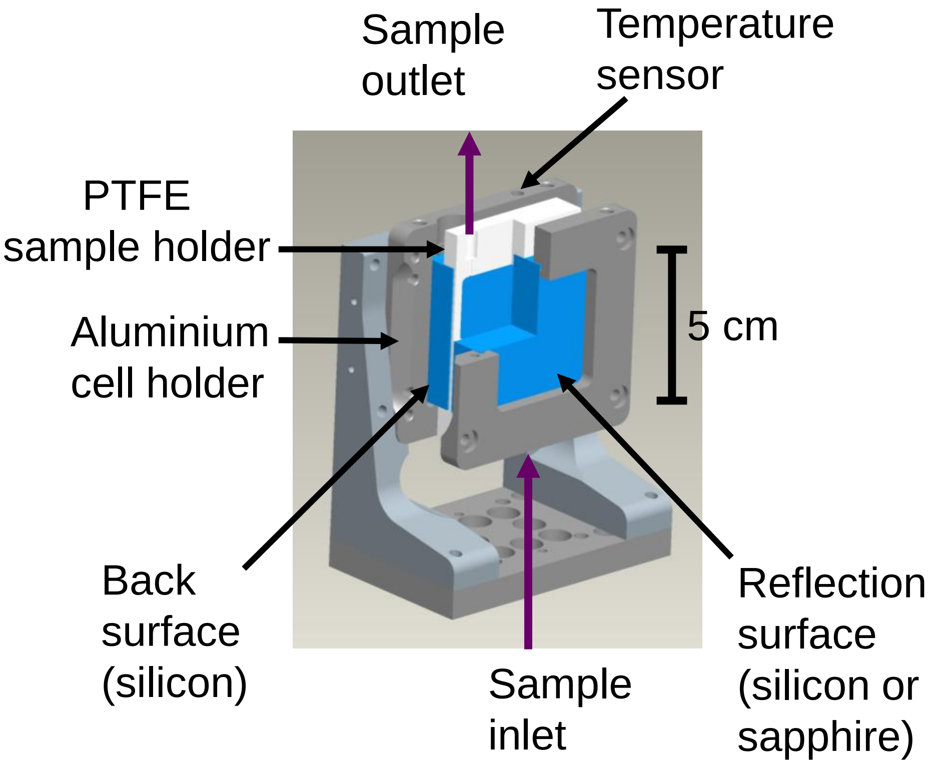
Effects of Resolution

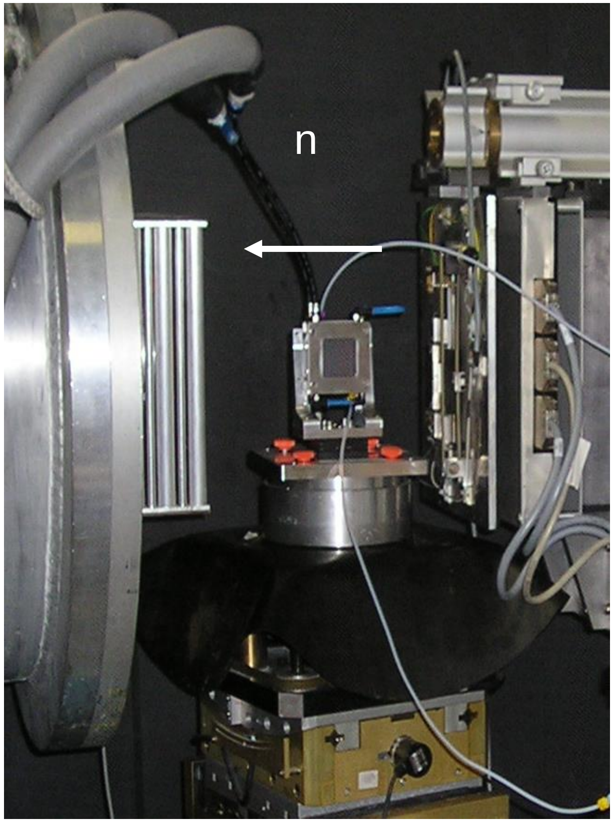


Silicon substrate: film thickness 1500 Å (150 nm)
scattering length density 6.3 × 10^{-6} Å^{-2}

Sample Holder

D17 reflectometer
ILL, France





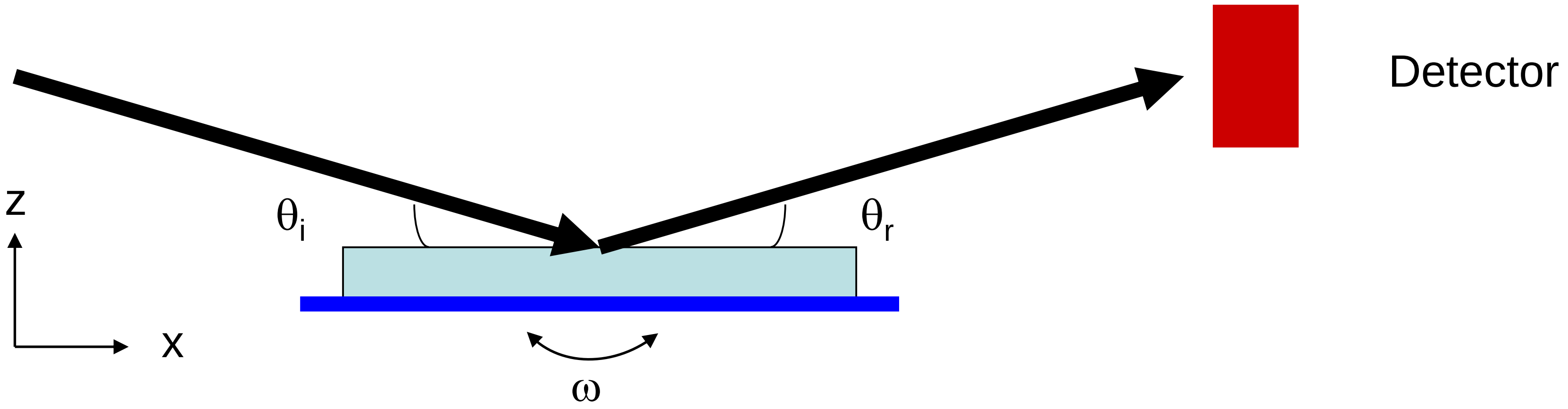
Alignment

Rotation table must have centre on beam axis

Sample must be centred on rotation (half obscure the direct beam) – eucentric mount

Determine θ from the position of beam on a detector

Aligning a Sample



Design mount with surface at centre of rotation of ω. Eucentric mount.

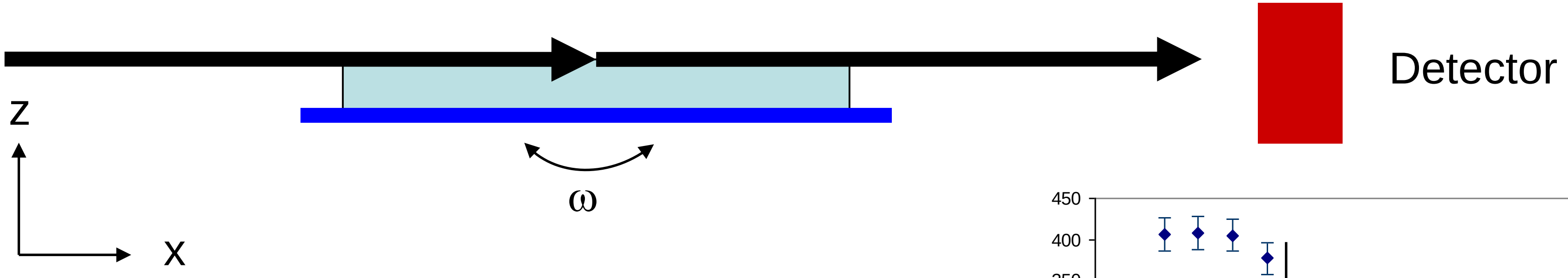
Put centre of surface on the line through axis of rotation (x direction)

The rotation ω stage must be centred on the incident beam.

Aligning a Sample

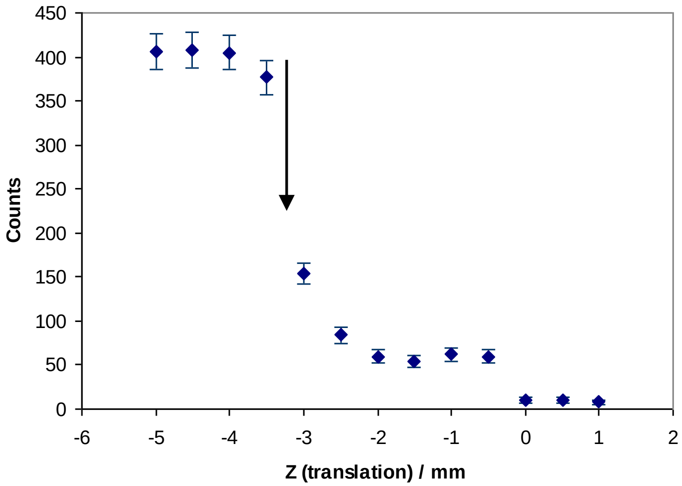
Set sample and detector to nominal zero

Choose fine slits to give collimated beam



Scan z

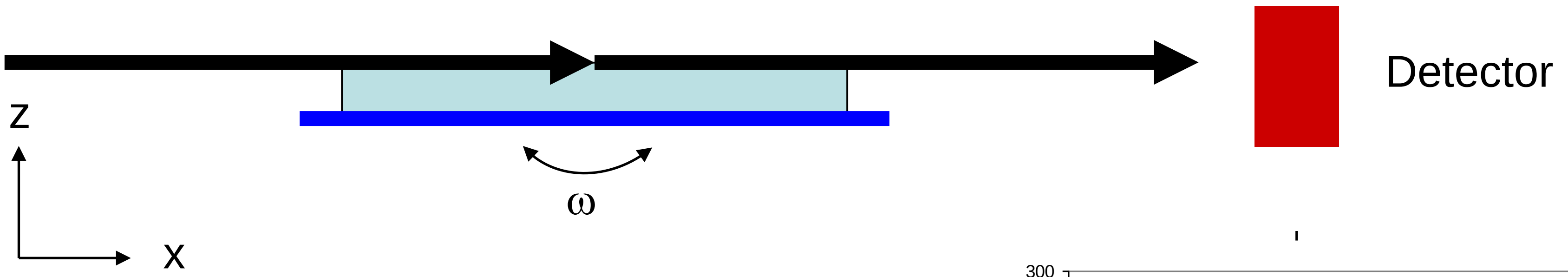
Look at intensity on detector



Identify z = -3.2 (~230 cts) as position interface intersects direct beam

Aligning a Sample

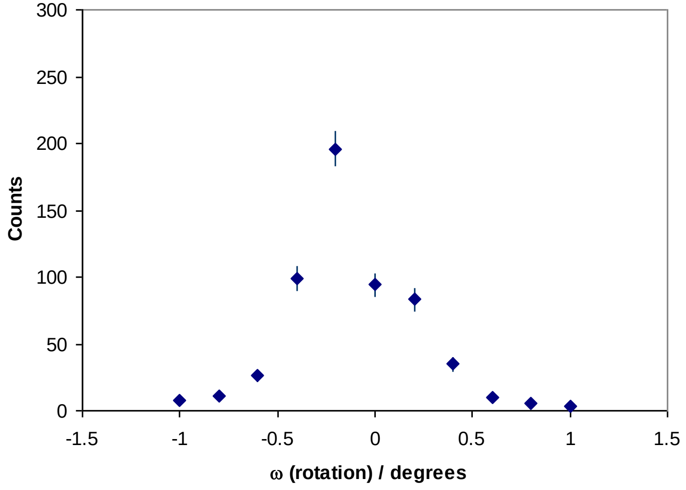
Move z to approximate sample in beam position



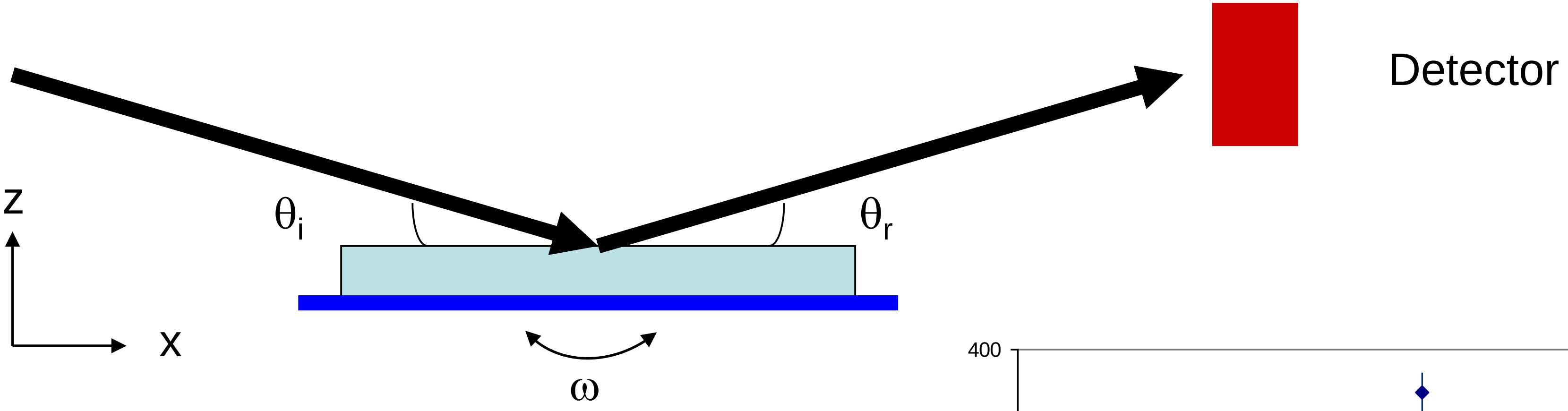
Scan ω

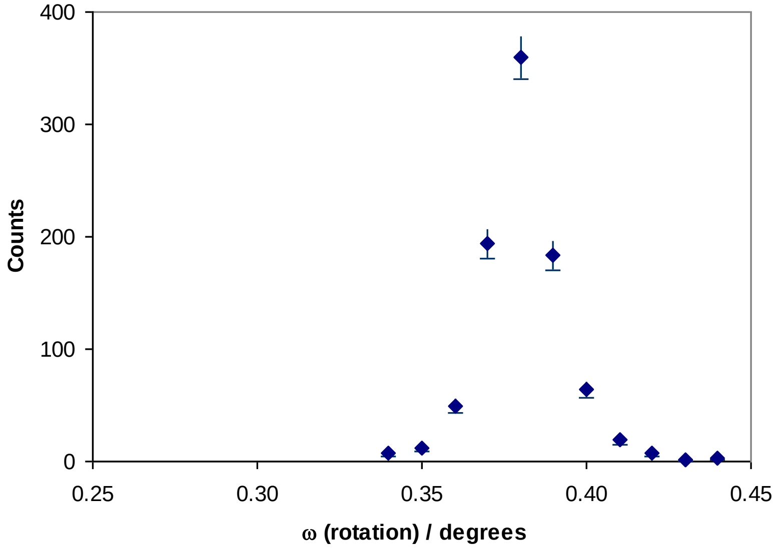
Look at intensity on detector

Identify ω = -0.22 (~190 cts) as approximate sample offset angle



Aligning a Sample



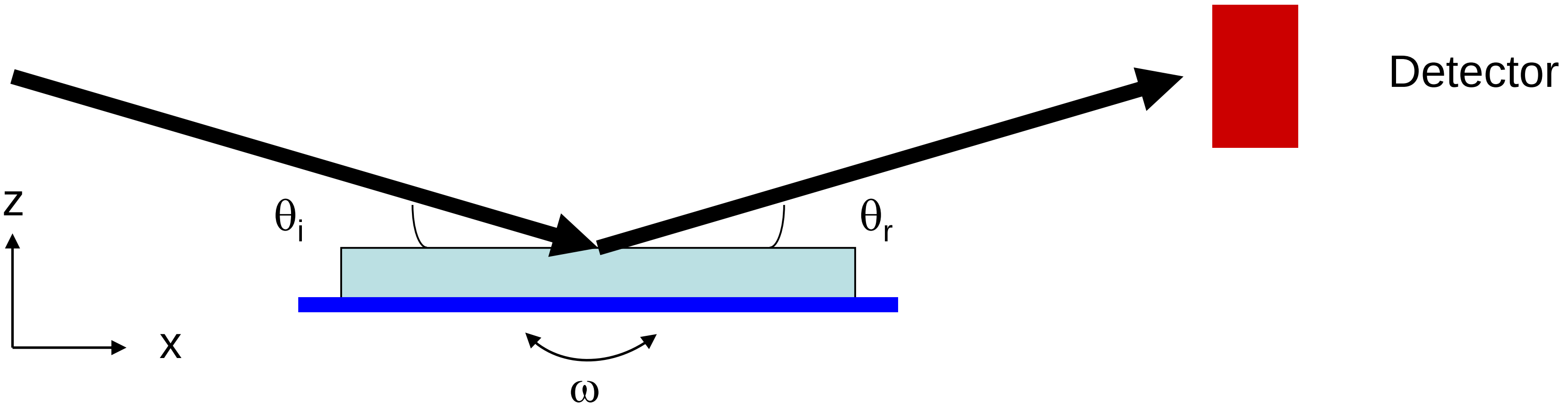


Use approximate ω and z offset from alignment on direct beam

Set detector to small angle of reflection (e.g. 0.5°) and align more precisely.

Scan ω and look for peak. Position is 0.378° and so offset is -0.122°.

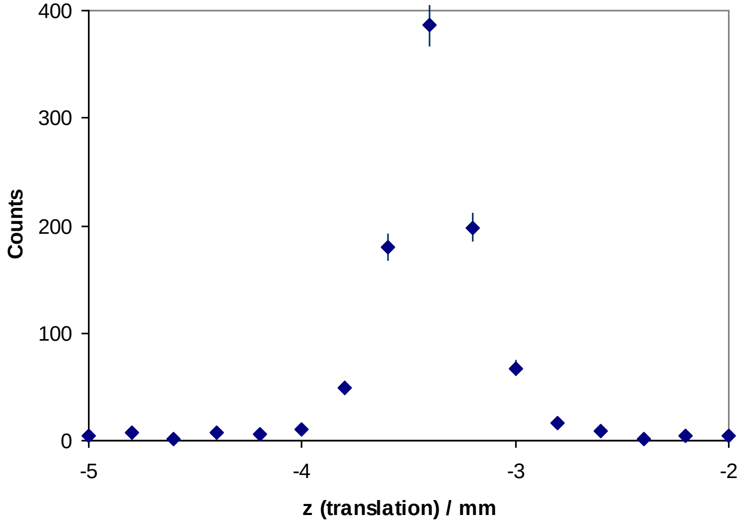
Aligning a Sample



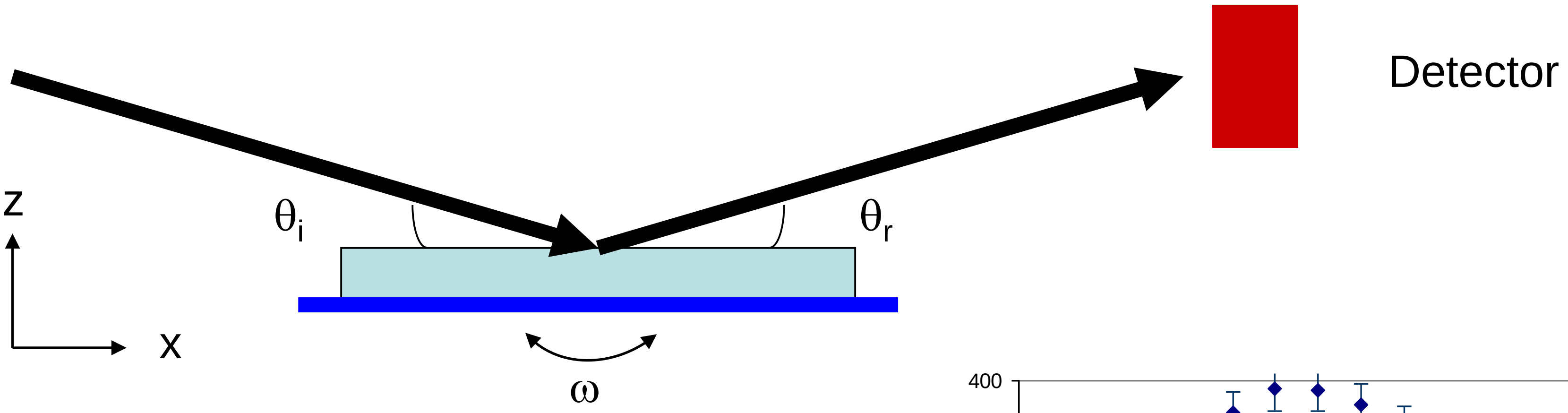
Use new ω offset and z offset from alignment on direct beam

Check translation (z) offset in reflection mode.

Scan z and look for peak. Position is -3.38 mm.

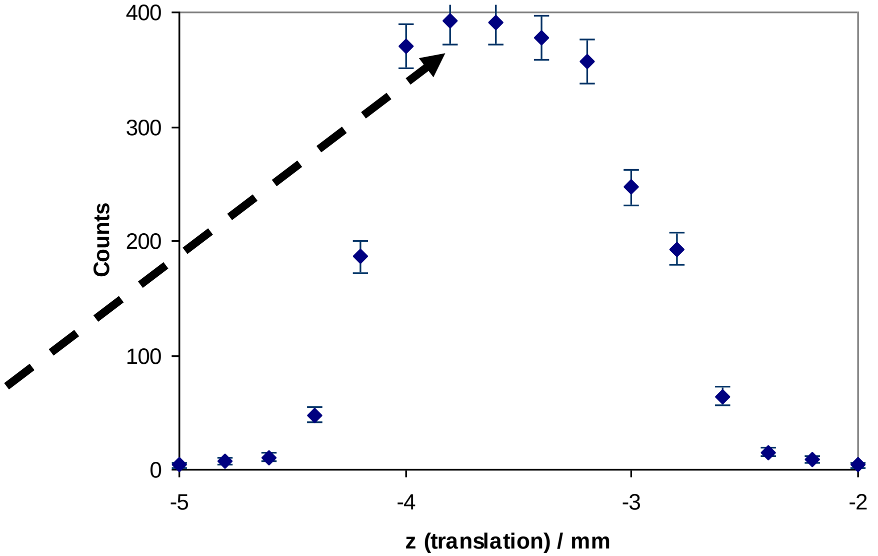


Comments on Alignment



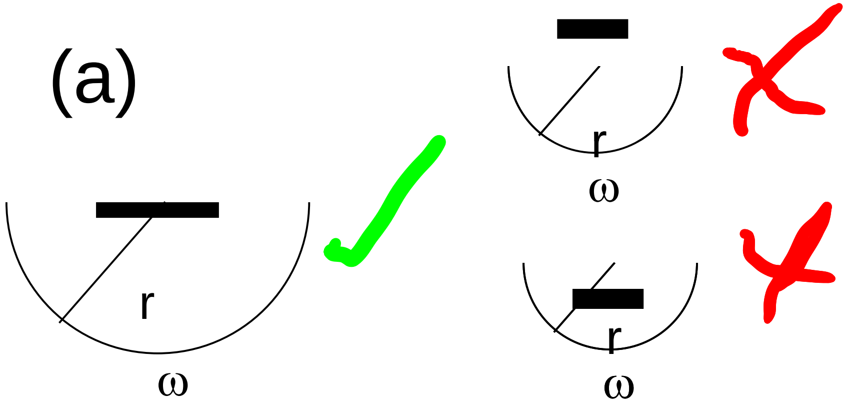
Angular (ω) width can depend on flatness of sample as well as resolution from slits and wavelength spread

If sample is very under-illuminated, translation (z) scan will have a flat top



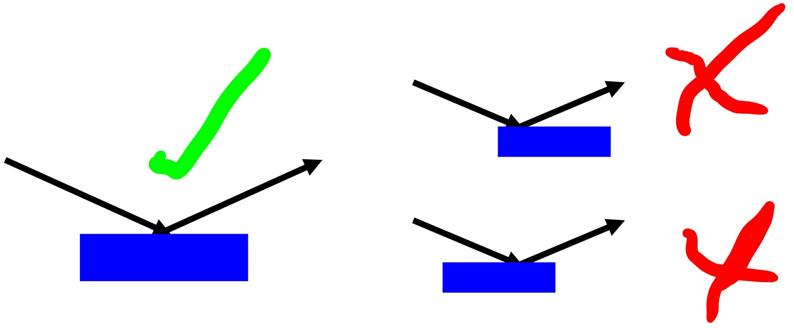
Summary - Mounting and Alignment

(a)



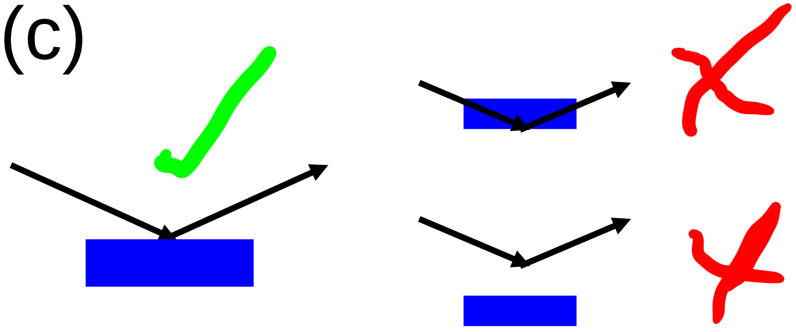
Eucentric mount

(b)



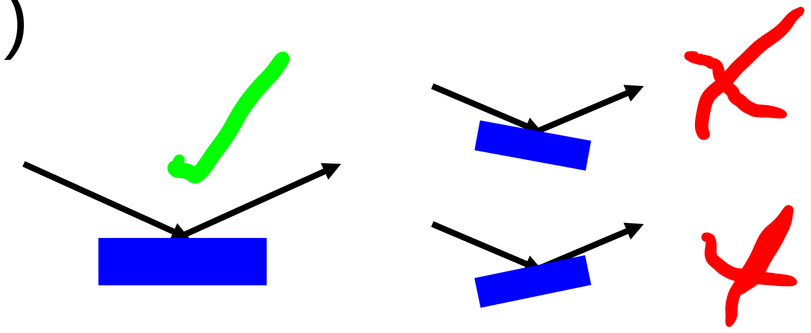
Centred on beam

(c)



z position correct

(d)



ω offset correct

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Comments on Alignment

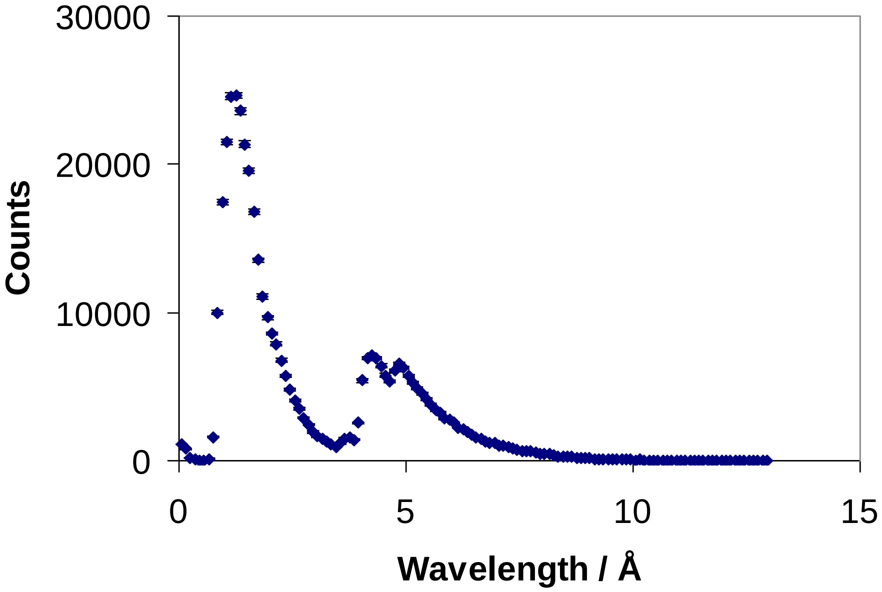
Using the results of alignment scans needs offsets or new zero positions to be set on the instrument. Warning: there is no general convention of signs on different instruments

Linear thermal expansion can be ~2 x 10^{-5} K^{-1}. 4 cm of aluminium changed by 50 C gives a shift of 0.04 mm.

Calibrations

Scan angle, measure different λ or a combination of λ and angle

Measure direct beam (through sample environment if needed)



Incident beam spectrum, LARMOR

Samples

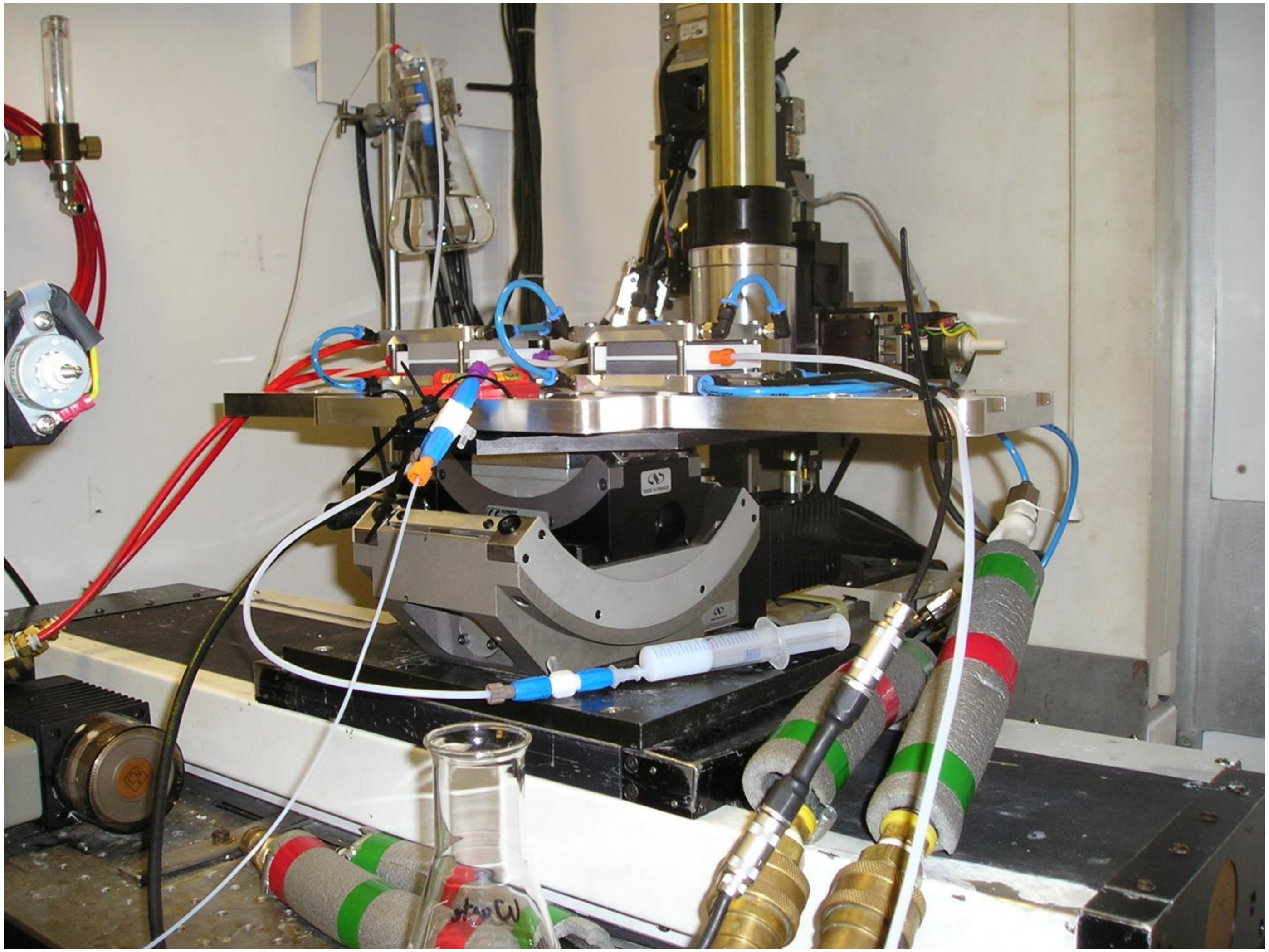
Low incident angle requires large uniform surface area. Footprint ~ s / tan θ.

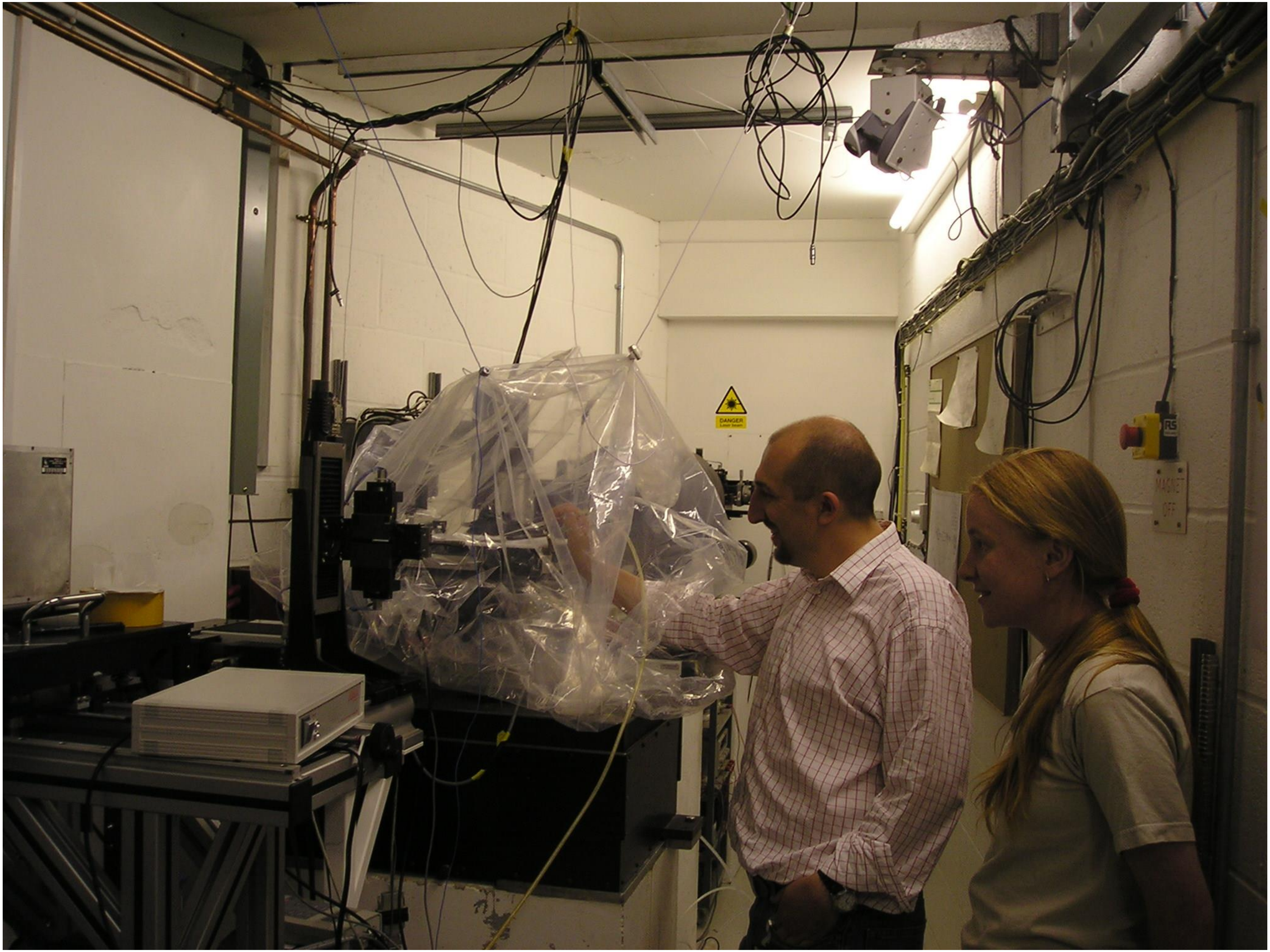
Areas often several cm^2.

Smooth surface. 10 Å roughness will reduce the reflectivity at q=0.1 Å^{-1} by 2.7. 15 Å reduces reflectivity by a factor of 10.

Liquids will have surface oscillations (capillary waves). Need to avoid other, induced waves.

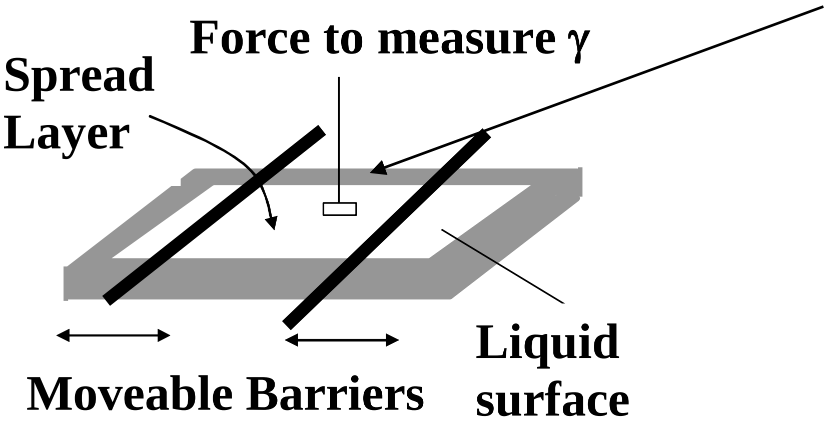
Sample Cell

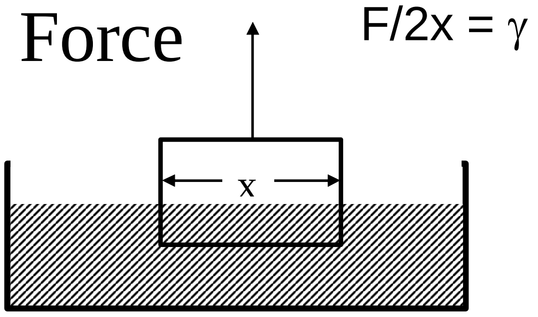



DANGER
Laser beam
RS
MAGNET
OFF

Chemistry on a Liquid Surface

Langmuir Trough





In place of a drop use, a uniform flat surface

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What is measured?

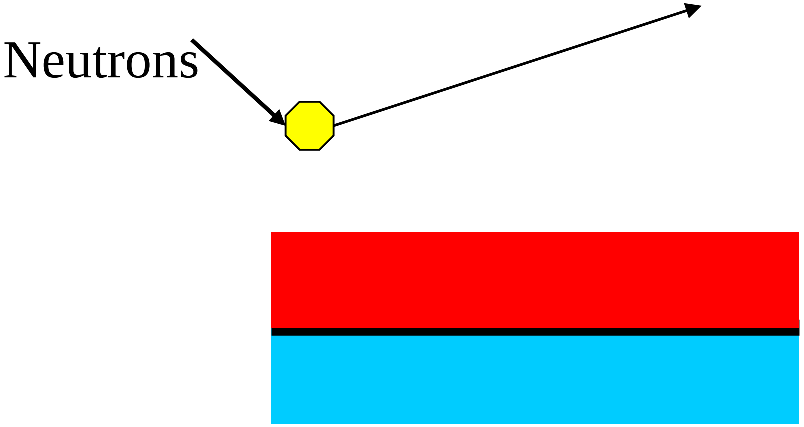
Reflected signal may have a large background

For hydrogenous substrate ~ 5 x 10^{-6} incident beam

Attenuation by reduced transmission (caused by scattering or absorption) may be significant

Fate of a Neutron at an Interface

- Reflected
- Scattered/Diffracted from surface
- Absorbed
- Scattered from bulk (either side of surface)
- Other accidents



What does background look like?

X-ray scattering – glass

Sinha et al., *Phys. Rev. B.* **38**, 2297, 1988.

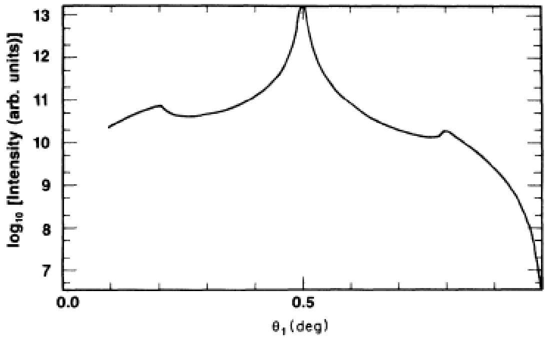
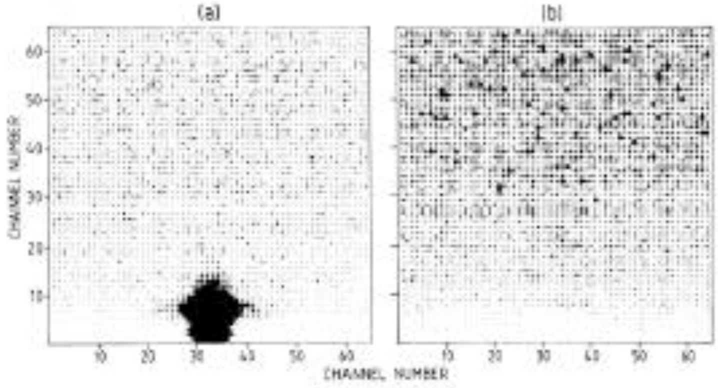


FIG. 6. Calculation of diffuse scattering in the distorted-wave Born approximation for rocking curve where θ_1 and θ_2 are varied such that 2θ is fixed at 1°. The asymmetry is due to the area of the illuminated surface decreasing as θ_1 is increased. The q_y direction has been integrated over. Parameters are $\sigma = 7$ Å, $h = 0.2$, $\xi = 7000$ Å, and the optical constants for Pyrex are given in Sec. V.

Neutron scattering from D_2O and from null reflecting water

Rennie et al., *Macromolecules* **22**, 3466-3475 (1989).



Contrast Matching

H_2O $\rho = -0.56 \times 10^{-6}$ Å^{-2}

D_2O $\rho = +6.35 \times 10^{-6}$ Å^{-2}

$y \times 6.35 + (1-y) \times (-0.56) = 0$

$6.91\,y = 0.56$ or $y = 0.56 / 6.91 = 0.081$

i.e. 8% by volume of D_2O in H_2O has n = 1

Comments on Calculations

Programs that lose data

It is common to use logaritmic scales but background subtraction can give negative data points. R Q^4 is useful.

Experimental issues

Resolution – often needs to be included

Illumination

Small samples are often not able to reflect all the beam and a geometrical correction is applied.

Absolute reflectivity

Data is constrained if it is on an an absolute scale

What has not (yet) been covered?

Ellipsometry and X-rays

  Needs more calculations for *s* and *p* waves

How to write a minimisation routine?

How to install your favourite program?

Specific examples of real samples etc.

Do’s and Don’ts

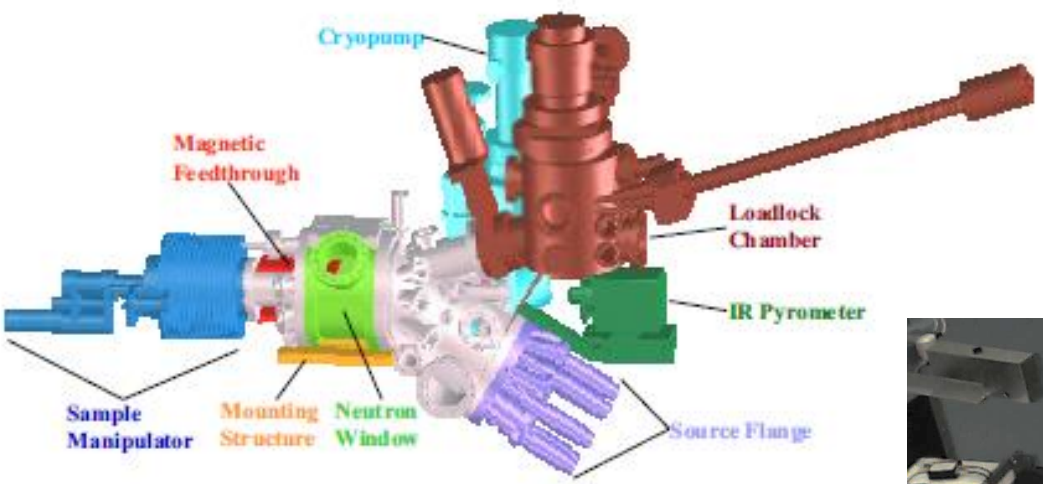
- Do not bend samples – care with mounts
- Use anti-vibration mounts for liquids – air borne noise causes vibrations
- Capillary waves cause scattering

Questions?

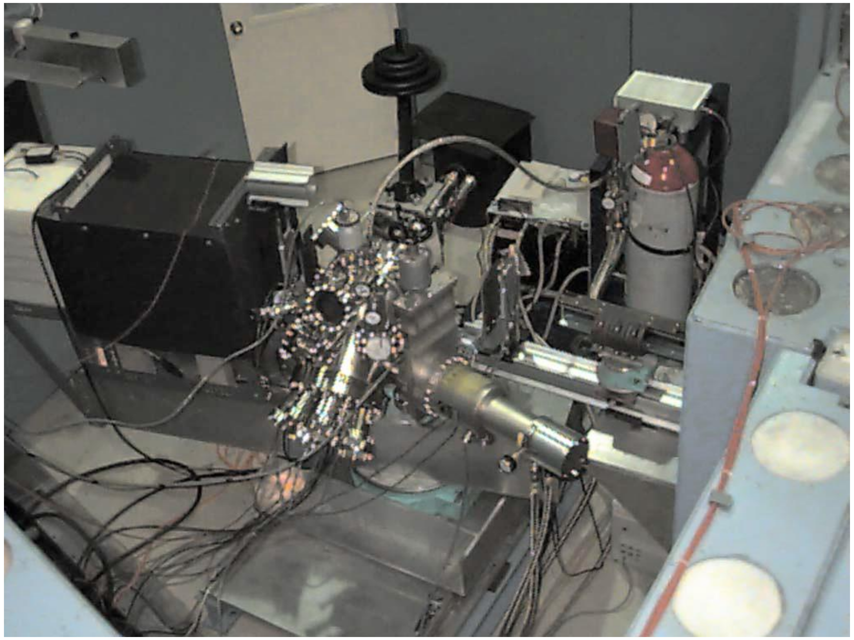
Sample Environments

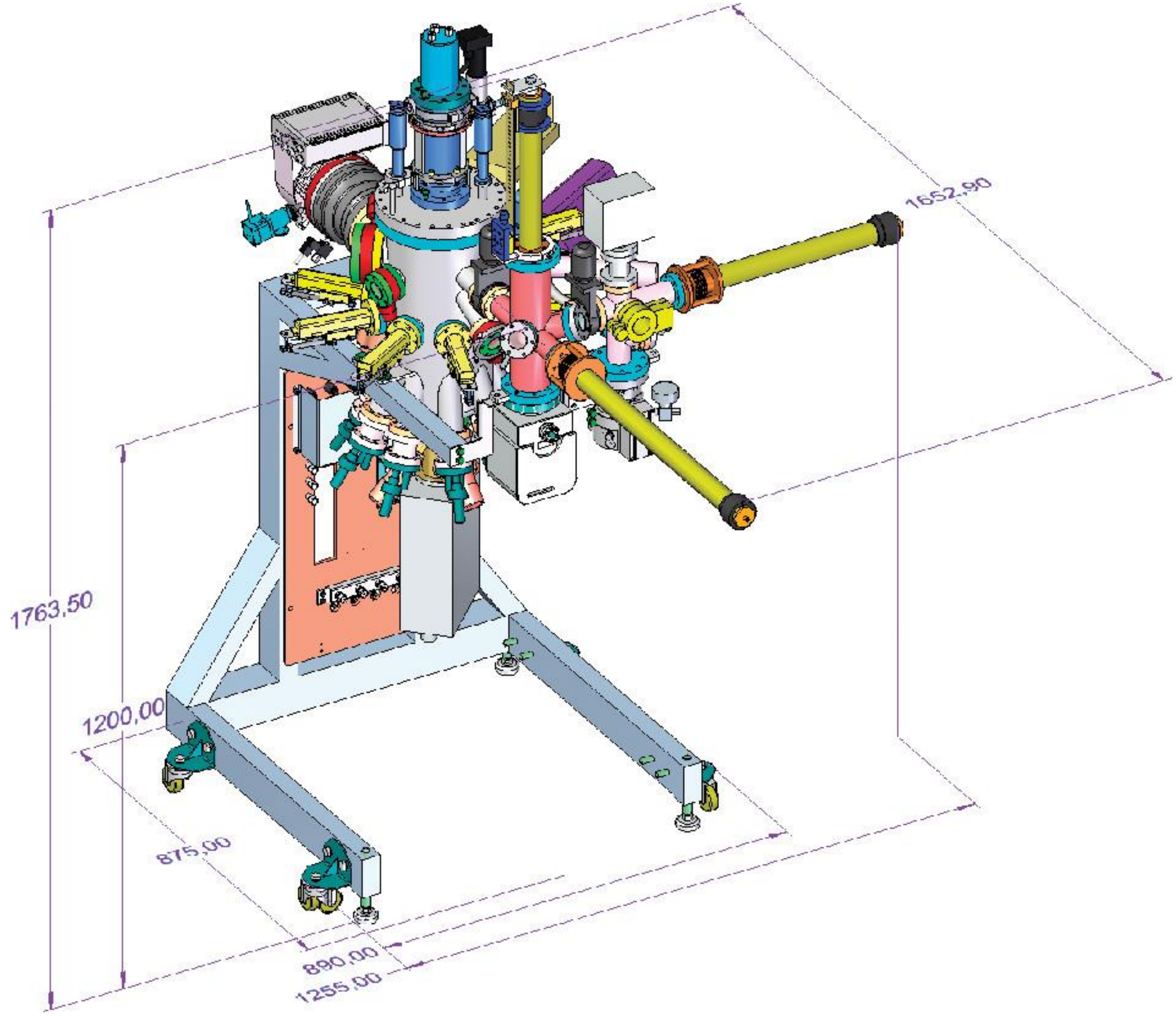
- Choice is very large
- Build for your own experiment

Thin Film Growth



J. A. Dura, J. LaRock ‘A molecular beam epitaxy facility for in situ neutron scattering’ *Rev. Sci. Instrum*. **80**, (2009), 073906.

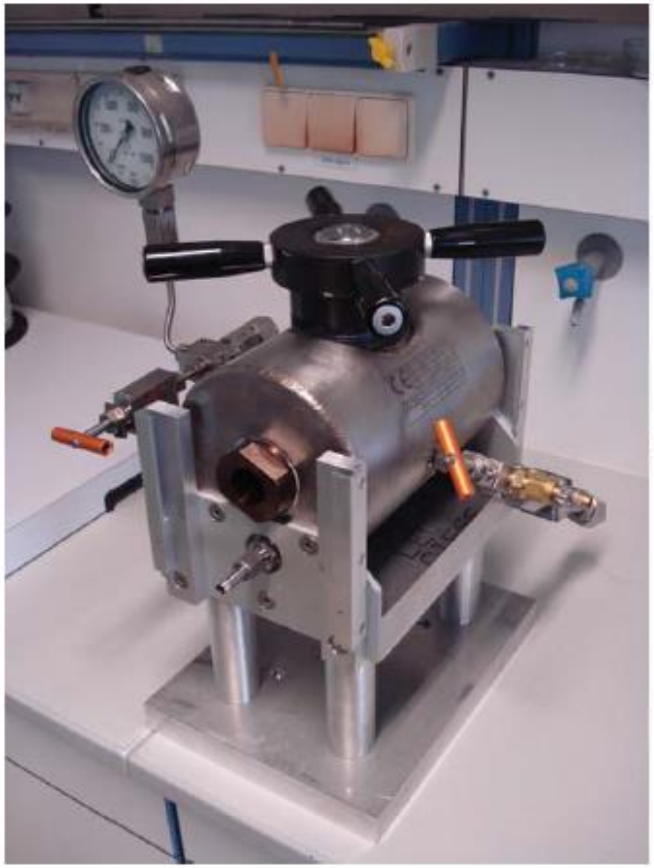


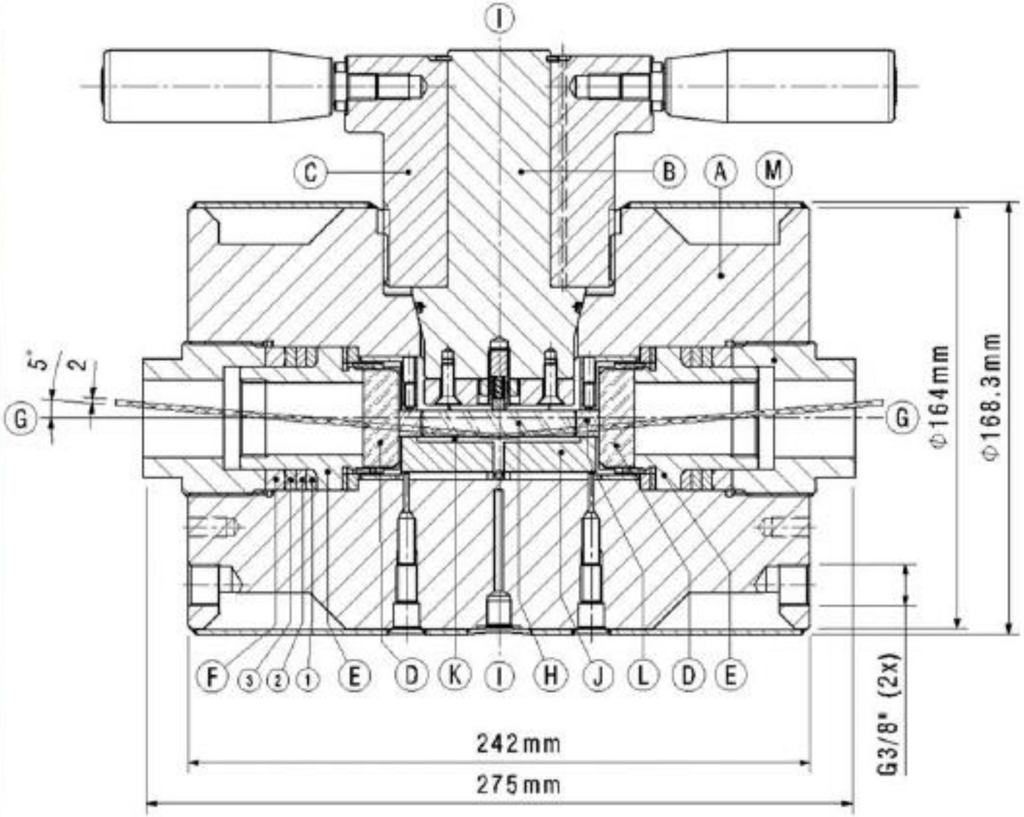


A. A. Baker, W. Braun, G. Gassler, S. Rembold, A. Fischer, T. Hesjedal ‘An ultra-compact, high-throughput molecular beam epitaxy growth system’ *Review of Scientific Instruments* **86**, (2015), 043901.

High Pressure

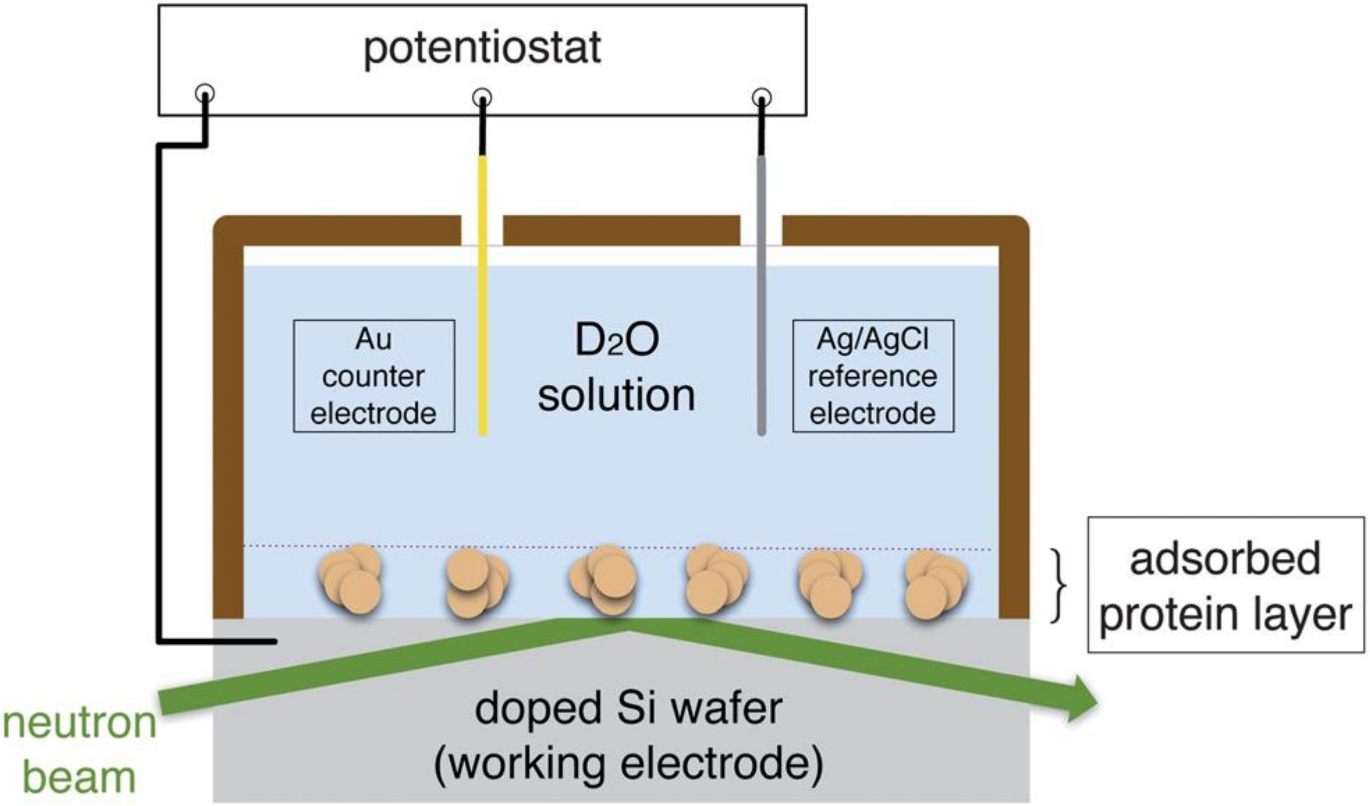
U





Martin Kreuzer, Thomas Kaltofen, Roland Steitz, Beat H. Zehnder, Reiner Dahint ‘Pressure cell for investigations of solid–liquid interfaces by neutron reflectivity’ *Rev. Sci. Instrum*. **82**, (2011), 023902.

Electric Potential and Electric Currents



Alexandros Koutsioubas, Didier Lairez, Gilbert Zalczer, Fabrice Cousin ‘Slow and remanent electric polarization of adsorbed BSA layer evidenced by neutron reflection’ *Soft Matter*, **8**, (2012), 2638-2643.

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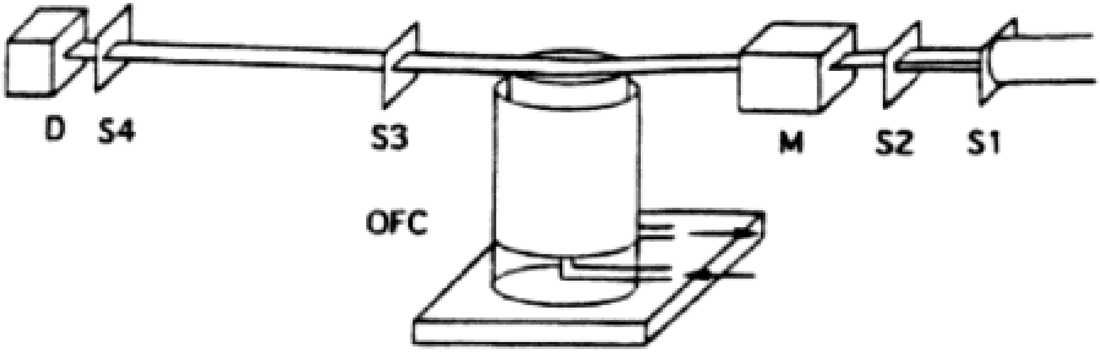
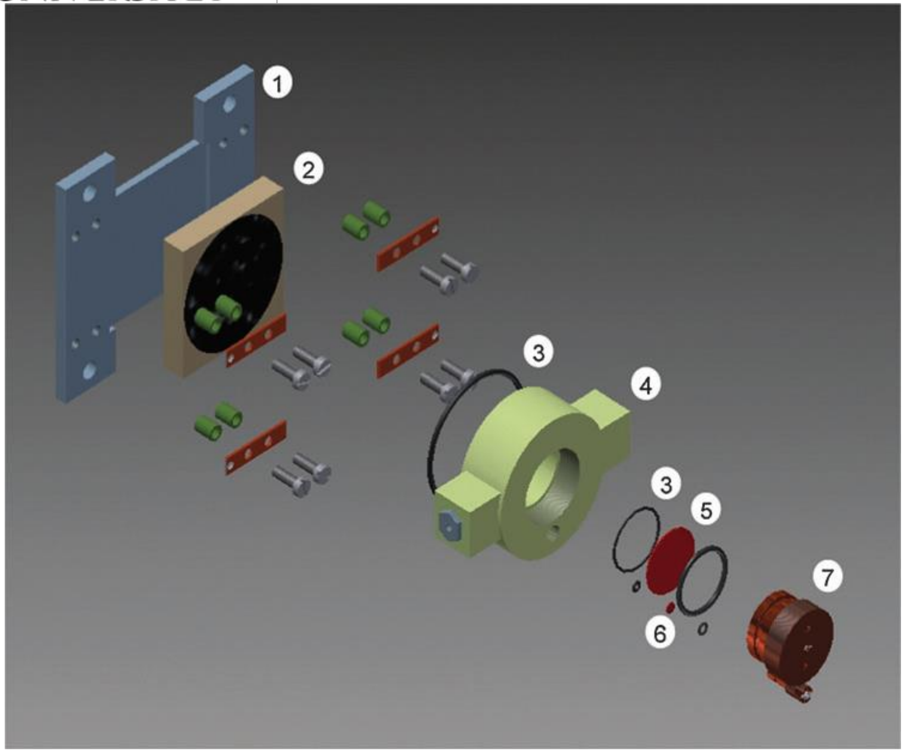
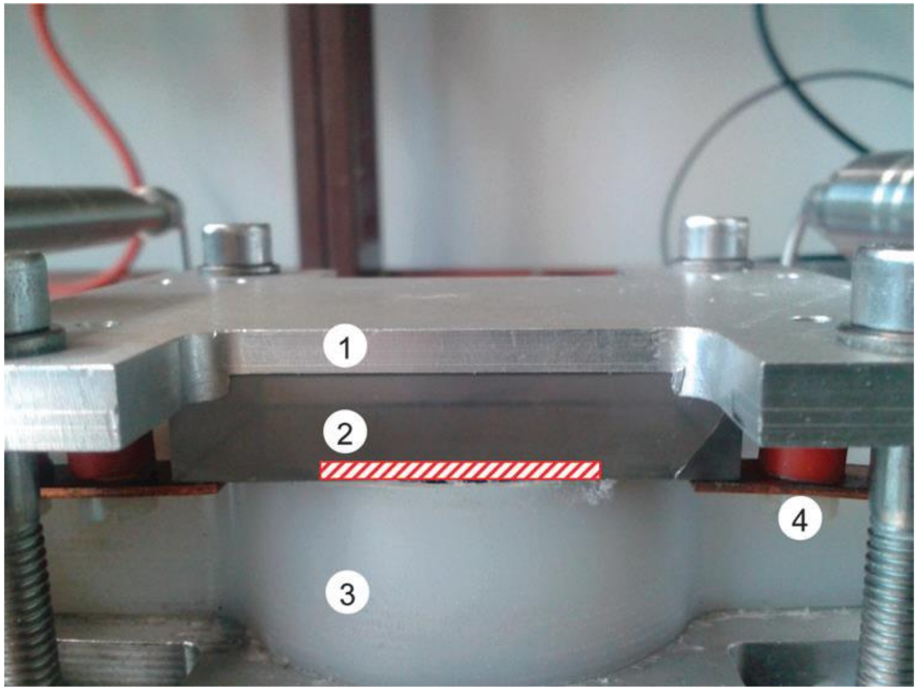
Continuously Generated Fresh Liquid Surface



Julian Eastoe, Alex Rankin, Ray Wat, Colin D. Bain, Dmitrii Styrkas, Jeff Penfold ‘Dynamic Surface Excesses of Fluorocarbon Surfactants’ *Langmuir*, **19**, (2003), 7734-7739.

Battery Electrodes





B. Jerliu, L. Dörrer, E. Hüger, G. Borchardt, R. Steitz, U. Geckle, V. Oberst, M. Bruns, O. Schneider, H. Schmidt ‘Neutron reflectometry studies on the lithiation of amorphous silicon electrodes in lithium-ion batteries’ *Phys. Chem. Chem. Phys*., **15**, (2013), 7777-7784.

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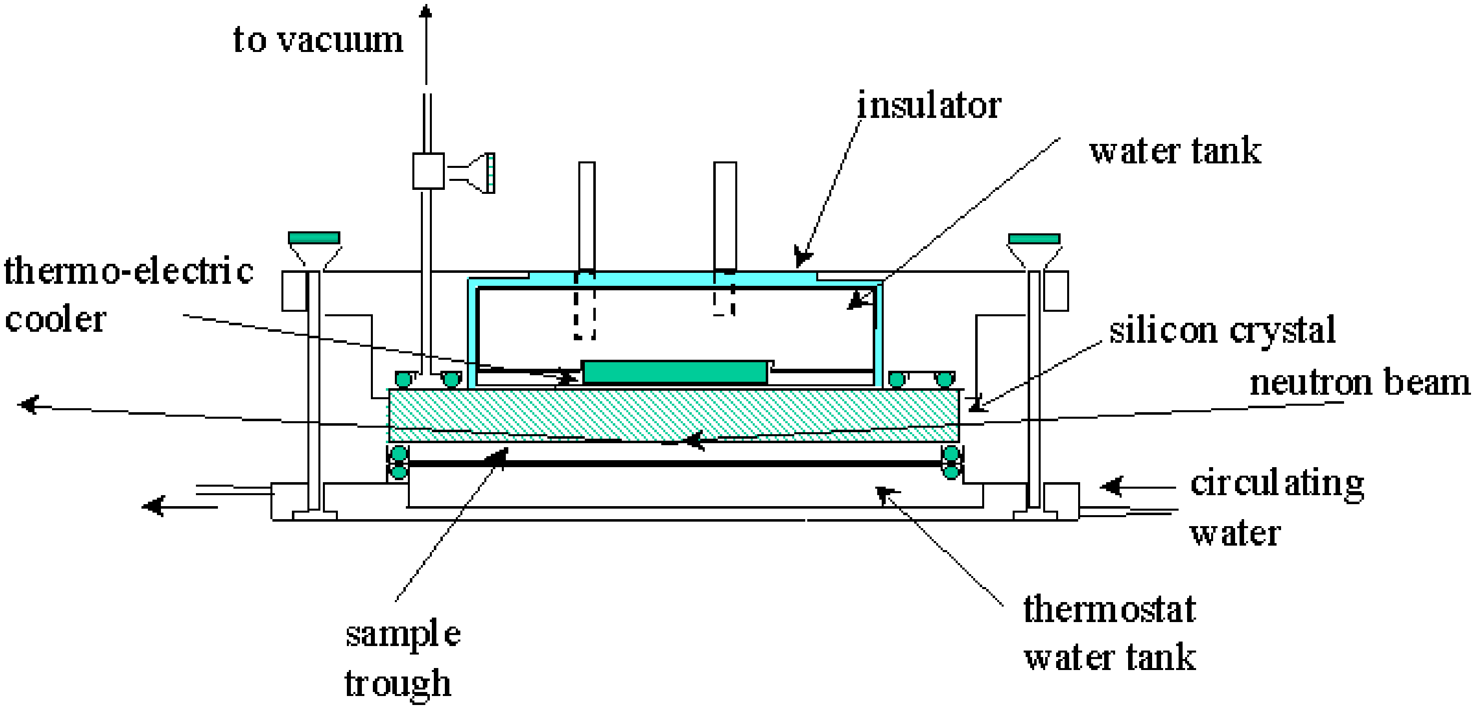
Liquid / Liquid Interfaces



A. Zarbakhsh, J. Bowers, J. R. P. Webster, ‘A new approach for measuring neutron reflection from a liquid/liquid interface’ *Meas. Sci. Technol*. **10**, (1999), 738-743.

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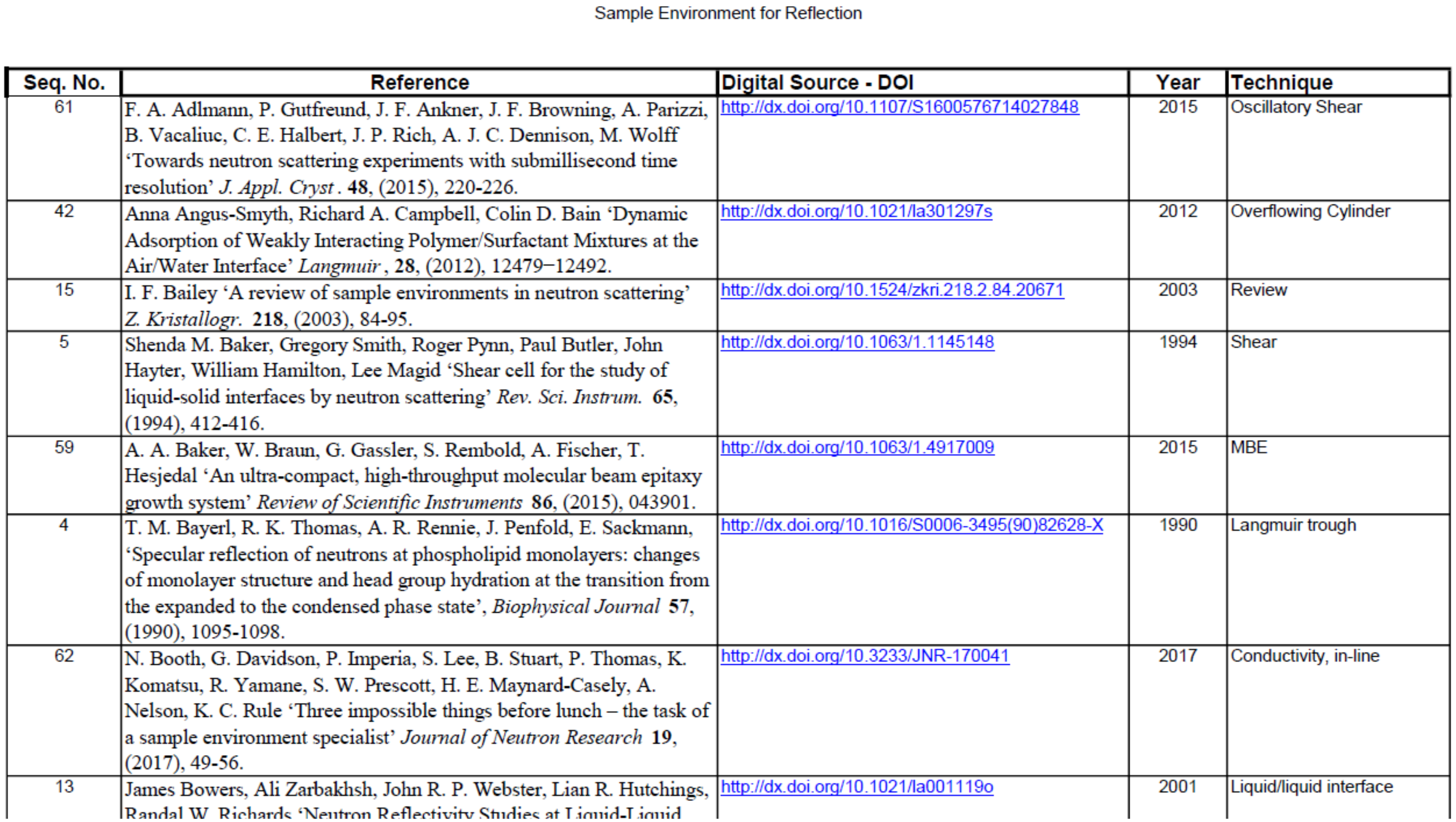
Other Ideas and Possibilities

http://www.reflectometry.net/reflect_bib.htm#Sample_environment



Sample Environment for Reflection

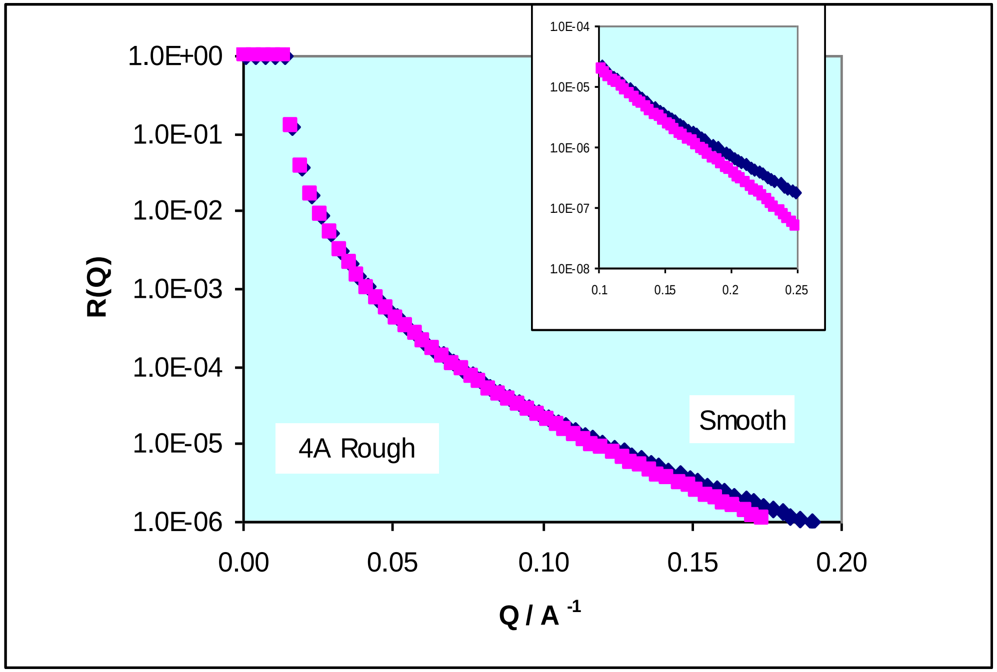
Seq. No.	Reference	Digital Source - DOI	Year	Technique
61	F. A. Adlmann, P. Gutfreund, J. F. Ankner, J. F. Browning, A. Parizzi, B. Vacaliuc, C. E. Halbert, J. P. Rich, A. J. C. Dennison, M. Wolff 'Towards neutron scattering experiments with submillisecond time resolution' *J. Appl. Cryst* . **48**, (2015), 220-226.	http://dx.doi.org/10.1107/S1600576714027848	2015	Oscillatory Shear
42	Anna Angus-Smyth, Richard A. Campbell, Colin D. Bain 'Dynamic Adsorption of Weakly Interacting Polymer/Surfactant Mixtures at the Air/Water Interface' *Langmuir* , **28**, (2012), 12479−12492.	http://dx.doi.org/10.1021/la301297s	2012	Overflowing Cylinder
15	I. F. Bailey 'A review of sample environments in neutron scattering' *Z. Kristallogr.* **218**, (2003), 84-95.	http://dx.doi.org/10.1524/zkri.218.2.84.20671	2003	Review
5	Shenda M. Baker, Gregory Smith, Roger Pynn, Paul Butler, John Hayter, William Hamilton, Lee Magid 'Shear cell for the study of liquid-solid interfaces by neutron scattering' *Rev. Sci. Instrum.* **65**, (1994), 412-416.	http://dx.doi.org/10.1063/1.1145148	1994	Shear
59	A. A. Baker, W. Braun, G. Gassler, S. Rembold, A. Fischer, T. Hesjedal 'An ultra-compact, high-throughput molecular beam epitaxy growth system' *Review of Scientific Instruments* **86**, (2015), 043901.	http://dx.doi.org/10.1063/1.4917009	2015	MBE
4	T. M. Bayerl, R. K. Thomas, A. R. Rennie, J. Penfold, E. Sackmann, 'Specular reflection of neutrons at phospholipid monolayers: changes of monolayer structure and head group hydration at the transition from the expanded to the condensed phase state', *Biophysical Journal* **57**, (1990), 1095-1098.	http://dx.doi.org/10.1016/S0006-3495(90)82628-X	1990	Langmuir trough
62	N. Booth, G. Davidson, P. Imperia, S. Lee, B. Stuart, P. Thomas, K. Komatsu, R. Yamane, S. W. Prescott, H. E. Maynard-Casely, A. Nelson, K. C. Rule 'Three impossible things before lunch – the task of a sample environment specialist' *Journal of Neutron Research* **19**, (2017), 49-56.	http://dx.doi.org/10.3233/JNR-170041	2017	Conductivity, in-line
13	James Bowers, Ali Zarbakhsh, John R. P. Webster, Lian R. Hutchings, Randal W. Richards 'Neutron Reflectivity Studies at Liquid-Liquid	http://dx.doi.org/10.1021/la001119o	2001	Liquid/liquid interface

Questions?

Roughness

Reflectivity from rough surfaces is decreased.

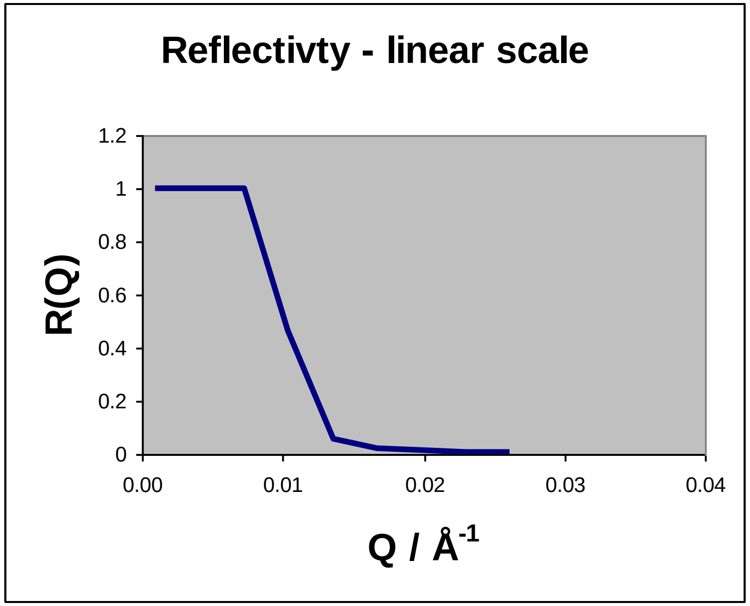
'Gaussian' roughness' – intensity decreases by $\exp(-Q^2\xi^2/2)$ for scattering vector, Q and amplitude of roughness, ξ.



L. Nevot, P. Crocé *J. Phys. Appl.* **15**, T61 (1980)

Critical Angle and Below (critical wavelength and above)

Density difference between two bulk phases determines the critical momentum transfer/angle, Q_c or θ_c



Any variation in intensity below critical angle is probably telling you about the experiment rather than the interface

$R = 1$ for $\theta < \theta_c$ is often used as a calibrant

Total reflection below critical angle θ

$$\cos\theta = n_2/n_1$$

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Intensity of Reflected Signal

- Waves interfere constructively for

$$2\,d \sin\theta = \lambda, 2\lambda, 3\lambda \ldots$$

- Measured reflectivity will depend on angle and wavelength. Add wave amplitudes with allowance for phase and calculate intensity as square of amplitude.
- Total reflection for angles less than critical angle, $\theta_c = \arccos(n_1/n_2)$

Fresnel Formula

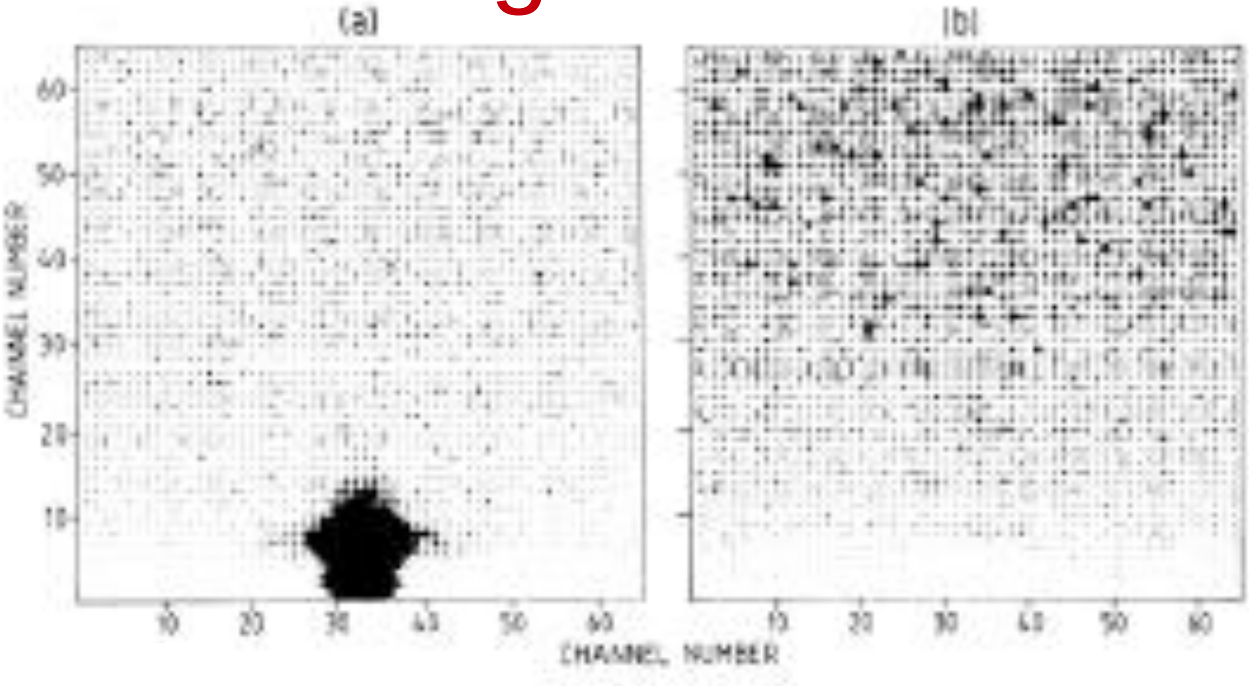
Reflection from an interface between two media with $\Delta\rho = \rho_1 - \rho_2$ is for $Q >> Q_c$:

$$R(Q) = 16\,\pi^2\,(\Delta\rho)^2 / Q^4$$

Note

This does not depend on sign of $\Delta\rho$.

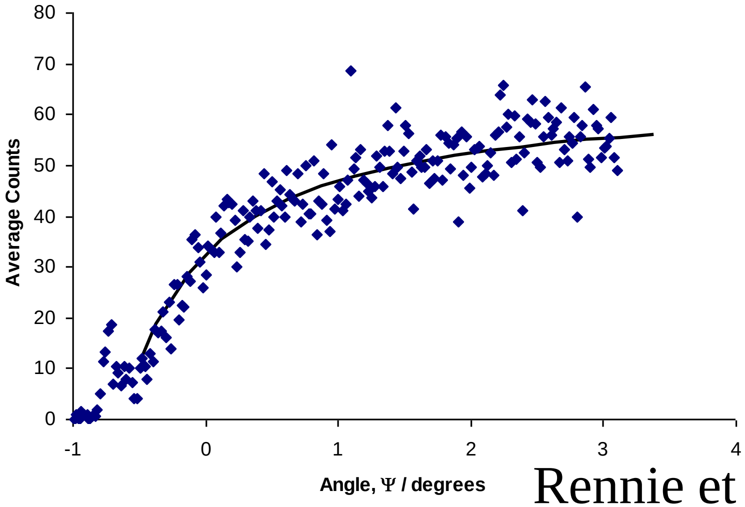
What does background look like?



Scattering from D_2O

and from null reflecting water

(8% D_2O)



Rennie et al., *Macromolecules* **22**, (1989), 3466-3475.